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REACTIONS OF SOME BASIC METAL CARBONYL DERIVATIVES

by



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## ABSTRACT

A number of salts of triphenylphosphonium cyclopentadienylide tricarbonyl molybdenum have been synthesised by oxidative addition of halogen or main Group IV metal halides to the free ylid. These compounds have the general formula  $[\text{CpylidMo}(\text{CO})_3\text{X}]^+\text{X}^-$  or  $\text{MX}_3^-$  where  $\text{X} = \text{Br}, \text{I}$  and  $\text{M} = \text{Ge}, \text{Sn}$ . The presence of a metal trihalide anion in the main Group IV metal halide derivatives has been confirmed by infrared studies. Triphenylphosphonium cyclopentadienylide tricarbonyl molybdenum has also been found to react with the mercuric halides, giving compounds of the type  $\text{CpylidMo}(\text{CO})_3\text{HgX}_2$  where  $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ . These compounds have been shown to be simple Lewis base-Lewis acid adducts, rather than salts, through conductivity measurements.

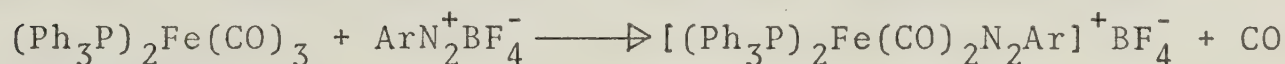
The base behaviour of some bisphosphine tricarbonyl iron compounds has been studied in detail. For  $(\text{Phos})_2\text{Fe}(\text{CO})_3$  ( $\text{Phos} = \text{Ph}_3\text{P}, \text{Ph}_2\text{MeP}$  and  $\text{PhMe}_2\text{P}$ ), treatment with nitrosonium hexafluorophosphate in acetonitrile has been found to produce either a complex nitrosyl cation  $[(\text{Phos})_2\text{Fe}(\text{CO})_2\text{NO}]^+ \text{BF}_4^-$  ( $\text{Phos} = \text{Ph}_3\text{P}$ ) or a neutral dinitrosyl derivative  $(\text{Phos})_2\text{Fe}(\text{NO})_2$  ( $\text{Phos} = \text{Ph}_2\text{MeP}, \text{PhMe}_2\text{P}$ ). The nmr spectra of these compounds corresponding to  $\text{X}_3\text{AA}'\text{X}_3'$  and  $\text{X}_6\text{AA}'\text{X}_6'$  systems, have been studied and compared with those of the bisphosphine tricarbonyl iron complexes.

For bistriphenylphosphine tricarbonyl iron, treatment with the diazonium tetrafluoroborates of aniline; o-, m-, and





p-toluidine; o-, m-, p-nitroaniline; p-anisidine; o-amino methyl benzoate; o-amino ethyl benzoate; and benzidine has been found to cause displacement of one carbon monoxide ligand from the molecule to give a complex arylazo salt.



The infrared data of these compounds are consistent with a trigonal bipyramidal structure about the central iron atom, the phosphine ligands occupying the axial positions, with the other ligands in the equatorial plane.

The position of the infrared active N-N stretching mode in these compounds (approx.  $1700\text{ cm}^{-1}$ ) has been confirmed by  $^{15}\text{N}$  substitution. These studies indicate the N-N bond order in these complexes to be closer to two than three. This is in accord with the postulate that the aryldiazonium cation  $\text{ArN}_2^+$  is a stronger  $\pi$ -acid but weaker  $\sigma$ -donor than CO.

Compounds of this type are felt to be specifically of interest as models for transition metal-nitrogen systems.





## ACKNOWLEDGEMENTS

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## CHAPTER III

Arylazo Derivatives of Bisphosphine Tricarbonyl  
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## -CHAPTER I

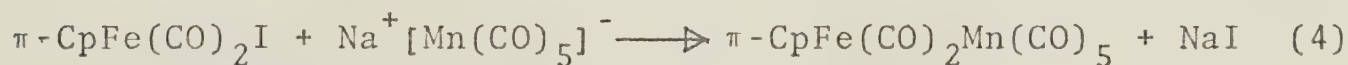
REACTIONS OF TRIPHENYLPHOSPHONIUM (MOLYBDENUM  
TRICARBONYL) CYCLOPENTADIENYLIDE WITH THE  
HALOGENS AND MAIN GROUP IV METAL HALIDES  
AND MERCURIC HALIDES

Introduction

The ability of many transition element atoms to function as bases in organometallic compounds, has long been recognized through the reactions of the common organometallic anions with organic halides and main Group IV metal halide derivatives.<sup>1</sup>



Similar reactions between these anions and other organometallic compounds are known to occur, resulting in the formation of metal-metal bonds between transition metals.



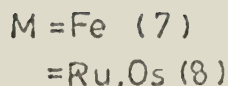
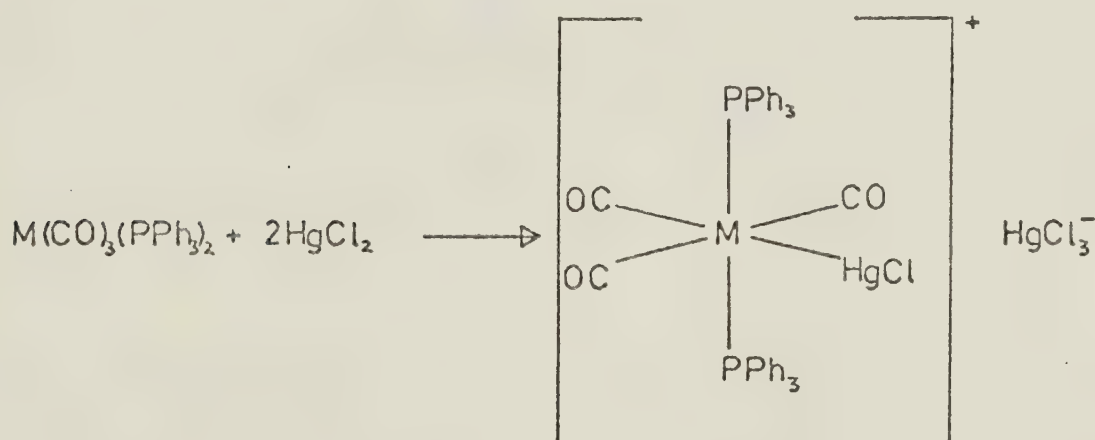
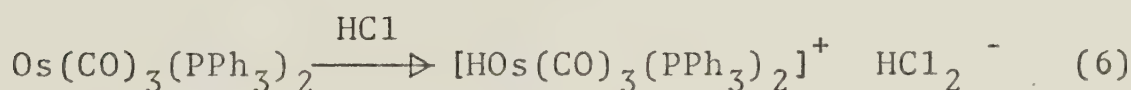
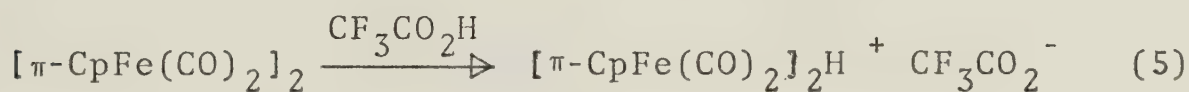
In all of these reactions, the anions may be regarded as Lewis bases, in which a lone pair of electrons is localized on the central metal atom. For transition metal organometallic compounds, these lone electron pairs are normally considered to be stereochemically inactive, unlike those of





ammonia, amines, water, etc. However, despite the lack of structural evidence for lone pairs of electrons, it is nevertheless useful to think of the organometallic anions as Lewis bases.

This type of base behaviour is not restricted to the organometallic anions. Many neutral organometallic compounds have also been found to react with Lewis acids such as the proton, and the mercuric halides.

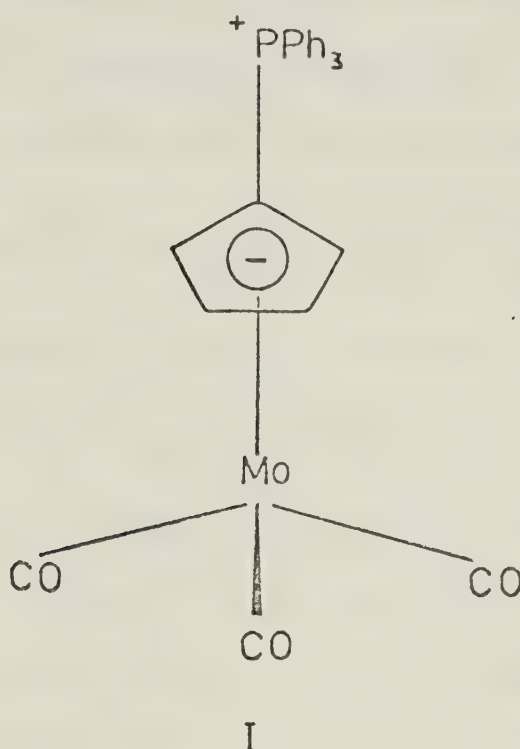


These compounds too may be regarded as Lewis bases, although again no stereochemically active lone electron pairs are known to arise. A neutral compound coming into this category,

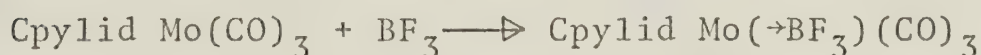
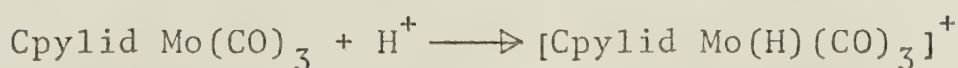


and one with which we will be concerned directly, is the complex, triphenylphosphonium (molybdenum tricarbonyl) cyclopentadienylide.

The basicity of the central metal atom in triphenylphosphonium (molybdenum tricarbonyl) cyclopentadienylide, (henceforth Cpylid  $\text{Mo}(\text{CO})_3$ ), (I) first prepared by

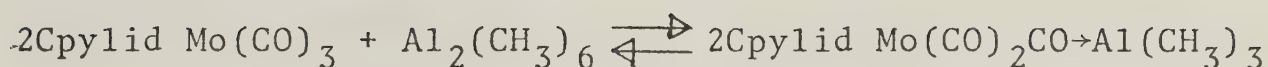


Wilkinson and co-workers,<sup>9</sup> has long been recognized through the reactions of the complex with strong acids, boron trifluoride,<sup>10</sup> and trimethylalane,<sup>11</sup> although evidence in this latter case favours an adduct formed via a terminal metal carbonyl group, rather than directly through the metal atom.



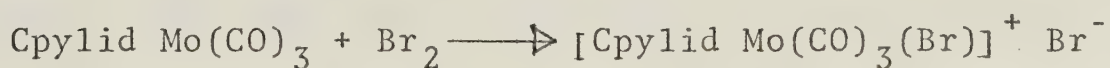




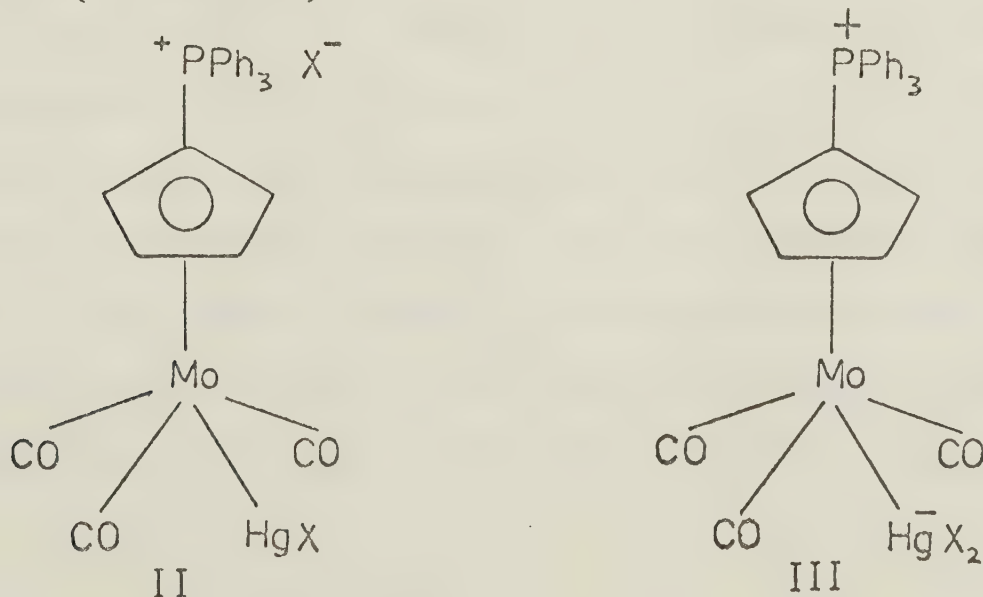


This, however, could be an anomalous reaction, since organoaluminum compounds are known to favour coordination to carbonyl oxygen rather than transition-metal atoms.<sup>12</sup>

More recently, Cashman and Lalor<sup>13</sup> have shown that the complex will undergo an oxidative addition reaction with bromine to form a reasonably stable 1:1 halide salt, as well as adducts with Lewis acids such as the mercury (II) halides.



In this study, the reactions with the halogens have been investigated further, and extended to include those with some of the main Group IV metal halides. In addition, the mercuric halide derivatives have been again prepared, in an attempt to elucidate whether or not they may be regarded as ionic compounds, or simple Lewis acid-Lewis base adducts (II and III).





## Results and Discussion

With the exception of the mercuric halide derivatives, isolation and purification of all the compounds prepared from Cpylid  $\text{Mo}(\text{CO})_3$  was hindered by the failure of these complexes to crystallize irrespective of the solvent systems used.

The halide salts obtained were prepared by direct reaction of the free halogen and Cpylid  $\text{Mo}(\text{CO})_3$  in a 1:1 molar ratio at room temperature in methylene chloride, under nitrogen. Only for the chloride was an excess of free halogen used, whilst for the iodide, care had to be taken that no excess of iodine was present, lest the tri-iodide anion be formed. In each case the reaction went almost instantaneously, with the solution rapidly changing colour from yellow to deep red. No gas evolution was observed.

In general, the reaction mixture was magnetically stirred for approximately twenty minutes to ensure completion, and the product then worked up by filtration of the solution and precipitation of the salt with a large excess of n-pentane. Due to the ionic nature of the product and the large anion-cation size difference, a series of oils was obtained. The iodide salt was isolated as a fine microcrystalline solid by recrystallization of the oil from acetone/diethyl ether. This method however, was unsuccessful when applied to the bromide and chloride. The latter proved to be too unstable as an oil to be well characterized, although the





former was characterized after all traces of solvent had been removed by keeping it under high vacuum (0.2mm pressure) for 48 hours. Treatment of each of the salts with sodium tetraphenylborate in methanol gave the tetraphenylborate salts, which were isolated as microcrystalline powders. Comparison of these compounds was facilitated by their greater overall stability, relative to the simple halide salts.

The halide derivatives of germanium (IV) and tin (IV) bromide and iodide were prepared in like manner. Again, it was found preferable to characterize all products as oils, rather than solids. Unfortunately the product of the reaction between  $\text{GeI}_4$  and Cpylid  $\text{Mo}(\text{CO})_3$  was found not to give the expected analytical results, even though its infra-red spectrum was consistent with the expected ionic derivative  $[\text{Cpylid Mo}(\text{CO})_3\text{I}]^+ \text{GeI}_3^-$ . Initially, this was thought to be due to some decomposition of germanium tetraiodide in the reaction solvent (methylene chloride). However, upon carrying out the reaction in methanol, in which  $\text{GeI}_4$  is both appreciably soluble and stable, a product was obtained which gave an analysis almost identical to that of the earlier sample. This was further found to be the case for a number of samples prepared in either methylene chloride or methanol, using  $\text{GeI}_4$  and Cpylid  $\text{Mo}(\text{CO})_3$  from different sources.

Adducts of the mercuric halides were prepared directly in dry acetone, from which they could easily be precipitated



by addition of a small amount of n-pentane, as microcrystalline powders. They proved to be fairly insoluble in most organic solvents, the decreasing order of solubility being Cpylid  $\text{Mo(CO)}_3\text{HgI}_2 > \text{Cpylid Mo(CO)}_3\text{HgBr}_2 > \text{Cpylid Mo(CO)}_3\text{HgCl}_2$ .

Analytical data for all compounds are given in Table I.

### Infrared Spectra

Assuming a zerovalent oxidation state for the central metal atom in the complex Cpylid  $\text{Mo(CO)}_3$ , it may be seen that the ylid ligand is formally required to be a six electron donor to the metal atom, in consequence of the effective atomic number rule. For this reason, although the ylid itself may be considered as a composite of the resonance forms<sup>14</sup>



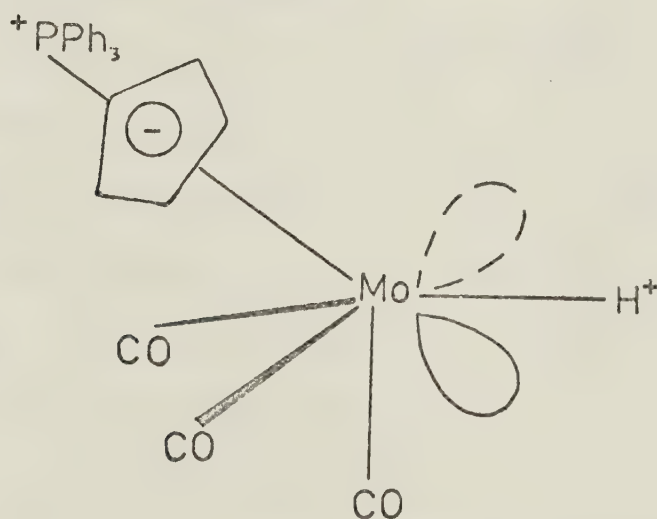
bonding to the Group IV transition metals is normally assumed to occur via form 'b', since this satisfies the electron requirements of the metal, while at the same time stabilizing the cyclopentadienyl ring of the ligand through enforced aromatic character. Evidence for the electron density thus imposed on the metal is provided by the low frequencies of the infrared active carbonyl stretching modes ( $\nu_{\text{CO}} = 1904$ ,





1808  $\text{cm}^{-1}$ ) of Cpylid  $\text{Mo}(\text{CO})_3$ , as compared with the isoelectronic compound benzenemolybdenum tricarbonyl ( $\nu_{\text{CO}} = 1991, 1919 \text{ cm}^{-1}$ ),<sup>15</sup> as well as by the tendency of the complex to form adducts, as mentioned previously.

The reason for the high negative charge imposed on the metal has been rationalized by Kotz and Pedrotty<sup>10</sup> for the protonated complex, assuming it to have bonding characteristics similar to bis( $\pi$ -cyclopentadienyl) metal hydrides (e.g.,  $\pi\text{-Cp}_2\text{ReH}$ ), which would require six valence electrons to remain on the metal following bonding to the ylid and carbonyl ligands. Presumably coordination of a proton then occurs via one of the three remaining pairs of electrons, giving a complex of  $C_s$  symmetry, (IV). Retention of this



IV

configuration in the unprotonated complex due to the presence



of stereochemically active lone electron pairs is, in our view, doubtful, since the carbonyl stretching modes of pure Cpylid  $\text{Mo}(\text{CO})_3$  exhibit two infrared-active bands both of which are symmetric in appearance, consistent with  $\text{C}_{3v}$  symmetry, instead of the three predicted from group theory for the structure of lower symmetry. (In actuality, if the substituent of the cyclopentadiene ring is considered, the symmetry of the complex must be regarded as  $\text{C}_s$ . However the deviation from pure  $\text{C}_{3v}$  symmetry is thought to be insufficient to cause splitting of the lower frequency adsorption into two bands, although it could explain the breadth of this band, as measured in solution.) Pure Cpylid  $\text{Mo}(\text{CO})_3$  is probably therefore best regarded as being fairly symmetric in structure (I) similar to the isoelectronic compound benzenetricarbonylmolybdenum.

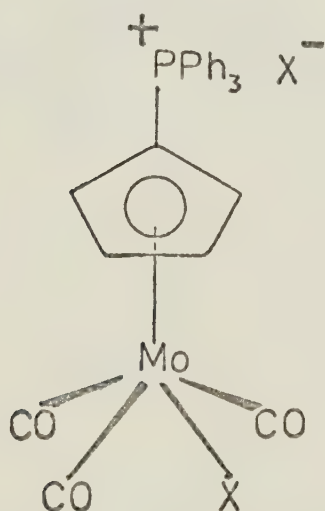
Generally, we have found that formation of halide salts, of Cpylid  $\text{Mo}(\text{CO})_3$  causes the ir active carbonyl modes to shift to higher frequencies, as might be expected due to the removal of electron density from the transition metal; at the same time, the lower-frequency carbonyl E mode broadens and frequently splits sufficiently to be resolved as two partially overlapping absorptions, even in methylene chloride. The positions of the carbonyl adsorptions are consistent with those observed previously for the bromide derivative.

The splitting of the lower-frequency carbonyl band is as expected for an overall reduction of molecular symmetry

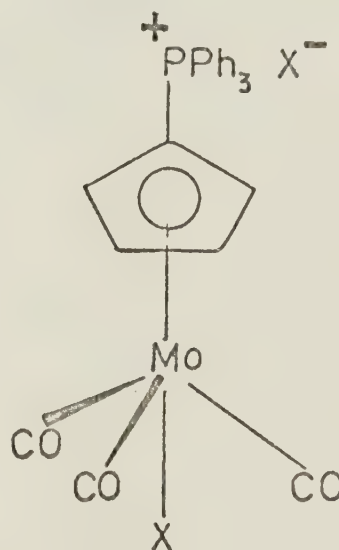




to  $C_5$ . Unfortunately no definite evidence is available as to the preferred configuration of any of these salts. Assuming a geometry based on seven coordination,<sup>16</sup> the ylid occupying three coordination sites, two structural possibilities arise, by comparison with the ethyl,<sup>17</sup> perfluoropropyl<sup>68</sup> and dimer<sup>69</sup> analogues of  $\pi\text{-CpMo(CO)}_3^-$ . One of these involves a 3:4 type coordination tetragonal-trigonal base in character, with the carbonyls and halide placed at the corners of the square and the ylid at the apex; the other involves a 3:3:1 or capped octahedral form, with the halide occupying the unique position, trans across the molecule to the ylid, (V and VI).



V



VI

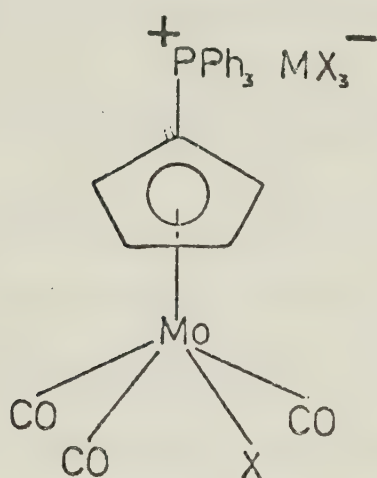
$X = \text{Cl, Br, I}$

Of these, the former seems the more likely, by analogy with  $\pi\text{-CpMo(CO)}_3\text{C}_2\text{H}_5$ .<sup>17</sup> However some distortion of the molecule away from this

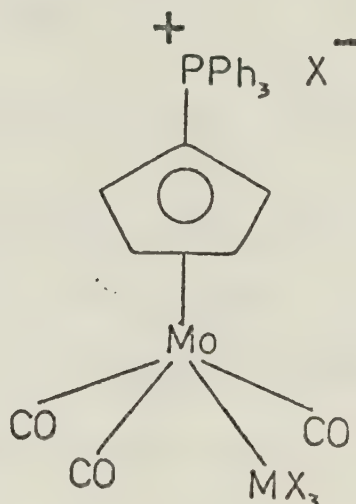


structure might occur, due to the bulkiness of the triphenylphosphine group attached to the cyclopentadiene ring.

The derivatives of the main Group IV metal halides may be formulated as salts in two ways, either with a simple halide anion, or with a more complex metal trihalide anion (VII and VIII). The close similarity of the infrared



VII



VIII

X = Br, I.  
M = Ge, Sn.

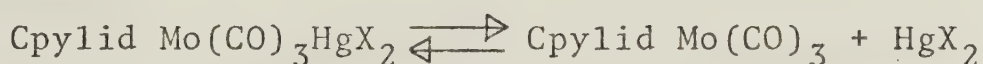
spectra of these compounds to those of the simple halide derivatives favours the latter formulation, however, since for a given X (V and VII) the cationic species is the same in either case. Hence similar infrared spectra would be expected.

For the mercury (II) halide adducts, splitting of the low frequency carbonyl E mode is again observed, with





separation of the two absorptions in general greater than that of the corresponding halides. The relative carbonyl band positions for the three complexes indicate the increasing order of Lewis acidity for the halides to be  $\text{HgCl}_2 \approx \text{HgBr}_2 > \text{HgI}_2$ . The ir spectra of these compounds in methylene chloride or nitrobenzene did not exhibit any carbonyl bands due to free Cpylid  $\text{Mo(CO)}_3$ , thus tending to rule out a dissociative equilibrium of the form:



which has been observed for other simple adducts of the mercuric halides.<sup>18</sup> This could be interpreted as evidence for the presence of 1:1 salts (i.e.,  $[\text{Cpylid Mo(CO)}_3\text{HgX}]^+\text{X}^-$ ) rather than pure adducts. (However, see below.)

### Conductivities

The conductivities in nitrobenzene solution (Table IV) of the products of reaction of Cpylid  $\text{Mo(CO)}_3$  and the halogens and main Group IV metal halides are all of the order expected for 1:1 salts.<sup>18</sup>

The conductivities of the  $\text{HgCl}_2$  and  $\text{HgBr}_2$  derivatives could not be measured with accuracy in either nitrobenzene or acetone due to their low solubilities. However, rough measurements indicate the conductivities of all solutions to be very close to those of the pure solvents; therefore, the adducts are essentially un-ionized. For the  $\text{HgI}_2$



derivative, the low molar conductivity value favours formulation of the compound as a simple Lewis acid-Lewis base adduct (III) rather than a salt (II). This would be in accord with the fact that reaction of Cpylid  $\text{Mo(CO)}_3$  with a two-fold excess of  $\text{HgI}_2$  only gives Cpylid  $\text{Mo(CO)}_3\text{HgI}_2$ , rather than  $[\text{Cpylid Mo(CO)}_3\text{HgI}]^+[\text{HgI}_3]^-$ . Similar behaviour with  $\text{HgBr}_2$  and  $\text{HgCl}_2$  has also been observed.

### Nmr Spectra

The nmr spectra of all compounds have been assigned in Table III. In most cases the AA'BB' resonance pattern of the protons of the substituted cyclopentadiene ring was not resolved, primarily due to the low solubilities of most derivatives in the solvents used to obtain spectra, resulting in weak signals.



## EXPERIMENTAL

All reactions were carried out in a nitrogen atmosphere. n-Pentane and n-hexane were dried over sodium, and methylene chloride over anhydrous magnesium sulphate. Diethyl ether was used as obtained from commercial sources.

Cpylid  $\text{Mo(CO)}_3$  was prepared by the method of Kotz and Pedrotty.<sup>10</sup> Triphenylphosphonium cyclopentadienylide was used as supplied by the Aldrich Chemical Company. Molybdenum hexacarbonyl, chlorine, bromine and iodine, and sodium tetraphenylboron were used as obtained from commercial sources, without further purification. The mercuric halides were used as obtained from the Fisher Scientific Company.

Tin(IV) bromide<sup>19</sup> and iodide,<sup>19</sup> and germanium(IV) bromide<sup>19</sup> and iodide<sup>19</sup> were prepared by standard methods.

Microanalyses were performed by the microanalytical laboratory of this department. Infrared spectra were measured using a Perkin-Elmer 337 grating spectrometer and recorded in expanded form on a Hewlett-Packard 7127 A recorder calibrated using either gaseous CO or DBr. Nmr measurements were made on Varian A56/60 A, Varian Ha-100-12, or Jeolco Minimar 60 instruments at  $40 \pm 2^\circ\text{C}$ . Conductivities were determined using a YSI 3400 series conductivity cell in conjunction with a Philips PR 9500 bridge.





Preparation of  $[\text{Cpylid Mo}(\text{CO})_3\text{X}]^+\text{X}^-$  or  $[\text{Cpylid Mo}(\text{CO})_3\text{X}]^+\text{MX}_3^-$   
where X = Br, I and M = Sn, Ge

Typically, a sample of halogen or metal halide (1mmole) was added directly to a solution of Cpylid  $\text{Mo}(\text{CO})_3$  (0.5gm, 1mmole) in methylene chloride (10 ml), and the mixture stirred rapidly for 20 minutes. After filtering, the product was brought out of solution by the addition of a large excess of n-pentane. The oil obtained was then shaken with small portions of diethyl ether (2 x 20 ml), the ether decanted, and the product dried under high vacuum (0.2 mm, 48 hrs). This procedure normally caused the oil to become a rather airy, slightly sticky solid, which despite its appearance was found to be satisfactory for analysis.

Other attempts to purify the products were less successful. Purification by chromatography could not be carried out, since the salts tended to be strongly adsorbed by even mild column bases such as silica gel. Recrystallization from solvent systems such as methylene chloride/n-pentane, methylene chloride/diethyl ether, methylene chloride/benzene, and acetone/diethyl ether was also unsuccessful, the product invariably coming out of solution as an oil, rather than a solid. The exception to this was the iodide derivative, which was successfully recrystallized from acetone/diethyl ether. Many of the derivatives of the main Group IV metal halides could be obtained as "semi-solids" by slow addition of a methylene chloride solution of the product to a large



excess of diethyl ether. The microcrystalline solids so formed were found, after filtration, to be, in actuality, coated with a thin film of oil, which made their removal from a sinter difficult. Thus despite the appearance of the product obtained, the most satisfactory method of isolation of these compounds was found to be that described above.

Preparation of  $[\text{Cpylid Mo(CO)}_3\text{X}]^+\text{B(C}_6\text{H}_5)_4^-$ , X = Cl, Br, I

Methylene chloride solutions of  $[\text{Cpylid Mo(CO)}_3\text{X}]^+\text{X}^-$  (X = Cl, Br, I) were prepared by the above method. (The chloride salt was obtained by passing chlorine gas into a methylene chloride solution of Cpylid  $\text{Mo(CO)}_3$ .) Following removal of solvent on a rotary evaporator, the product (1mmole) was dissolved in a small quantity of methanol (12 ml) and a solution of sodium tetraphenylborate (0.34g, 1mmole), dissolved in the minimum amount of methanol, added with stirring. A precipitate rapidly formed, which was filtered off, washed with cold methanol ( $0^\circ\text{C}$ , 2 x 2 ml) and dried under vacuum. (0.2 mm, 48 hrs.)

Preparation of  $\text{Cpylid Mo(CO)}_3\text{HgX}_2$ , X = Cl, Br, and I

A sample of mercuric halide (1 mmole) was added with stirring to an acetone (10 ml) solution of Cpylid  $\text{Mo(CO)}_3$  (0.5 g, 1mmole). Immediate reaction occurred, with some precipitation for the mercuric chloride derivative. Precipitation of the product was completed by the addition of n-pentane to





the acetone solution. The yellow solid obtained was filtered off, washed with diethyl ether (2 x 3 ml) and dried in vacuum. The mercuric iodide derivative could be further purified by recrystallization from methylene chloride/n-pentane.



TABLE I

Analytical Data and Physical Properties

Compound	Calculated %			Found %			% Yield <sup>a</sup>	Colour	Dec. Point
	C	H	X	C	H	X			
[CpylidMo(CO) <sub>3</sub> II] <sup>+</sup> I <sup>-</sup>	41.06	2.50	33.40	39.18	2.65	33.68	60.0	Light brown	72-78
[CpylidMo(CO) <sub>3</sub> Br] <sup>+</sup> Br <sup>-</sup>	46.86	2.85	33.40	45.28	3.10	23.85	83.3	Brown	Dec. above 70
[CpylidMo(CO) <sub>3</sub> II] <sup>+</sup> SnI <sub>3</sub> <sup>-</sup>	27.55	1.67	44.83	26.87	1.71	44.83	88.4	Red	102-105
[CpylidMo(CO) <sub>3</sub> II] <sup>+</sup> GeI <sub>3</sub> <sup>-</sup>	28.72	1.74	46.73	32.28	2.33	41.50	67.2	Red	Dec. above <sup>b</sup> 100
[CpylidMo(CO) <sub>3</sub> Br] <sup>+</sup> SnBr <sub>3</sub> <sup>-</sup>	33.04	2.01	33.85	33.01	2.45	34.49	72.1	Pink	94-119
[CpylidMo(CO) <sub>3</sub> Br] <sup>+</sup> GeBr <sub>3</sub> <sup>-</sup>	34.73	2.11	35.58	35.17	2.18	35.21	70.0	Orange	87-109
[CpylidMo(CO) <sub>3</sub> II] <sup>+</sup> BPh <sub>4</sub> <sup>-</sup>	63.04	4.09	13.33	62.83	4.28	13.43	55.0	Orange-red	Dec. above 100
[CpylidMo(CO) <sub>3</sub> Br] <sup>+</sup> BPh <sub>4</sub> <sup>-</sup>	66.32	4.31	8.83	66.57	4.53	8.62	48.5	Pale orange	Dec. above 100
[CpylidMo(CO) <sub>3</sub> Cl] <sup>+</sup> BPh <sub>4</sub> <sup>-</sup>	69.75	4.53	4.12	70.35	4.51	4.28	39.8	Pink	Dec. above 120

continued.....



Table I (continued)

CpylidMo(CO) <sub>3</sub> HgCl <sub>2</sub>	40.13	2.44	9.12	40.53	2.84	9.14	64.8	Pale yellow	Dec. above 170
CpylidMo(CO) <sub>3</sub> HgBr <sub>2</sub>	36.01	2.19	18.44	35.67	2.38	18.37	61.6	Pale yellow	Dec. above 177
CpylidMo(CO) <sub>3</sub> HgI <sub>2</sub>	32.48	1.97	26.42	31.93	2.08	26.43	52.3	Yellow	Dec. above 145

<sup>a</sup> Yield based on CpylidMo(CO)<sub>3</sub>

<sup>b</sup> This compound did not analyse correctly (see text).





TABLE II

Infrared Data<sup>a</sup>

Compound	$\nu_{\text{CO}}$ $\text{cm}^{-1}$	
$[\text{CpylidMo}(\text{CO})_3\text{I}]^+\text{I}^-$	2056 (s)	1889 (vs,br)
$[\text{CpylidMo}(\text{CO})_3\text{Br}]^+\text{Br}^-$	2064 (s)	1889 (vs,br)
$[\text{CpylidMo}(\text{CO})_3\text{I}]^+\text{SnI}_3^-$	2055 (s)	1882 (vs,br)
$[\text{CpylidMo}(\text{CO})_3\text{I}]^+\text{GeI}_3^-$	2054 (s)	1880 (vs,br)
$[\text{CpylidMo}(\text{CO})_3\text{Br}]^+\text{SnBr}_3^-$	2064 (s)	1992 (vs,br)
$[\text{CpylidMo}(\text{CO})_3\text{Br}]^+\text{GeBr}_3^-$	2065 (s)	1994 (vs,br)
$[\text{CpylidMo}(\text{CO})_3\text{I}]^+\text{BPh}_4^-$	2054 (s)	1884 (vs,br)
$[\text{CpylidMo}(\text{CO})_3\text{Br}]^+\text{BPh}_4^-$	2065 (s)	1997 (vs,br)
$[\text{CpylidMo}(\text{CO})_3\text{Cl}]^+\text{BPh}_4^-$	2070 (s)	1999 (vs,br)
$\text{CpylidMo}(\text{CO})_3\text{HgCl}_2$	1993 (w,br) 1977 (s)	1913 (w,br) 1926 (s)
$\text{CpylidMo}(\text{CO})_3\text{HgBr}_2$	1992 (s) 1976 (s)	1924 (s,br) 1925 (s)
$\text{CpylidMo}(\text{CO})_3\text{HgI}_2$	1988 (s) 1976 (s)	1918 (s,br)
		1903 (w,br) - Acetonitrile 1888 (s,br) - Nujol mull
		1905 (s,br) - Methylene chloride 1888 (vs,br) - Nujol mull
		1902 (s,br) - Methylene chloride 1880 (vs,vbr) - Nujol mull

<sup>a</sup> Taken in methylene chloride, unless otherwise recorded (0.5 mm KBr disc cells).



TABLE III

 $^1\text{H}$  Nmr Spectral Data

Compound	Solvent	$\tau_{\text{C}_6\text{H}_5}^a$	$\tau_{\text{C}_5\text{H}_4}^b$
$[\text{CpylidMo}(\text{CO})_3\text{I}]^+\text{I}^-$	$\text{CD}_2\text{Cl}_2$	2.07, 2.26	3.74
$[\text{CpylidMo}(\text{CO})_3\text{Br}]^+\text{Br}^-$	$\text{CD}_2\text{Cl}_2$	2.06	3.68
$[\text{CpylidMo}(\text{CO})_3\text{I}]^+\text{SnI}_3^-$	$\text{CD}_2\text{Cl}_2$	1.88, 2.10	3.56, 3.83
$[\text{CpylidMo}(\text{CO})_3\text{I}]^+\text{GeI}_3^-$	$\text{CD}_2\text{Cl}_2$	2.12, 2.32	3.82
$[\text{CpylidMo}(\text{CO})_3\text{Br}]^+\text{SnBr}_3^-$	$\text{CD}_2\text{Cl}_2$	1.84	3.42, 3.80
$[\text{CpylidMo}(\text{CO})_3\text{Br}]^+\text{GeBr}_3^-$	$\text{CD}_2\text{Cl}_2$	1.95	3.63, 3.90
$[\text{CpylidMo}(\text{CO})_3\text{I}]^+\text{BPh}_4^-$	$\text{CD}_2\text{Cl}_2$	2.46, 2.78, 3.22	c
$[\text{CpylidMo}(\text{CO})_3\text{Br}]^+\text{BPh}_4^-$	$\text{CD}_2\text{Cl}_2$	2.48, 2.80, 3.12, 3.22	c
$[\text{CpylidMo}(\text{CO})_3\text{Cl}]^+\text{BPh}_4^-$	$\text{CD}_2\text{Cl}_2$	2.46, 2.79, 3.22	c
$\text{CpylidMo}(\text{CO})_3\text{HgCl}_2$	Too insoluble for good spectra		
$\text{CpylidMo}(\text{CO})_3\text{HgBr}_2$	Too insoluble for good spectra		
$\text{CpylidMo}(\text{CO})_3\text{HgI}_2$	Too insoluble for good spectra		

continued.....



Table III (continued)

- a Peaks referred to are principal ones of a complex pattern.
- b Values refer to the halves of an AA'BB' pattern for the  $C_5H_4$  ring. This pattern was not normally resolved.
- c Pattern obscured by the  $BPh_4^-$  proton resonances.





TABLE IV

Compound	Conductivity Data <sup>a</sup>		Temperature
	Solution Conc. (mM)	Conductivity (mhos cm <sup>2</sup> moles <sup>-1</sup> )	
[CpylidMo(CO) <sub>3</sub> I] <sup>+</sup> I <sup>-</sup>	1.04	14.1	25.0
[CpylidMo(CO) <sub>3</sub> Br] <sup>+</sup> Br <sup>-</sup>	1.15	23.0	25.0
[CpylidMo(CO) <sub>3</sub> I] <sup>+</sup> SnI <sub>3</sub> <sup>-</sup>	1.06	23.2	25.5
[CpylidMo(CO) <sub>3</sub> I] <sup>+</sup> GeI <sub>3</sub> <sup>-</sup>	1.03	22.4	25.0
[CpylidMo(CO) <sub>3</sub> Br] <sup>+</sup> SnBr <sub>3</sub> <sup>-</sup>	0.95	19.7	25.0
[CpylidMo(CO) <sub>3</sub> Br] <sup>+</sup> GeBr <sub>3</sub> <sup>-</sup>	0.98	23.3	25.5
[CpylidMo(CO) <sub>3</sub> I] <sup>+</sup> BPh <sub>4</sub> <sup>-</sup>	1.11	21.0	25.5
[CpylidMo(CO) <sub>3</sub> Br] <sup>+</sup> BPh <sub>4</sub> <sup>-</sup>	0.96	19.0	25.5
[CpylidMo(CO) <sub>3</sub> Cl] <sup>+</sup> BPh <sub>4</sub> <sup>-</sup>	1.03	22.9	25.5
CpylidMo(CO) <sub>3</sub> HgCl <sub>2</sub>	low	approx. 0.0	25.5
CpylidMo(CO) <sub>3</sub> HgBr <sub>2</sub>	low	approx. 0.0	25.5
CpylidMo(CO) <sub>3</sub> HgI <sub>2</sub>	0.98	1.7	25.5

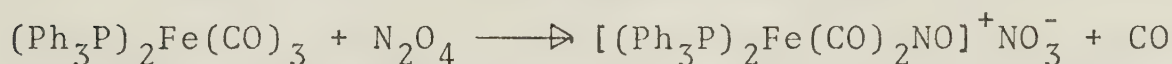
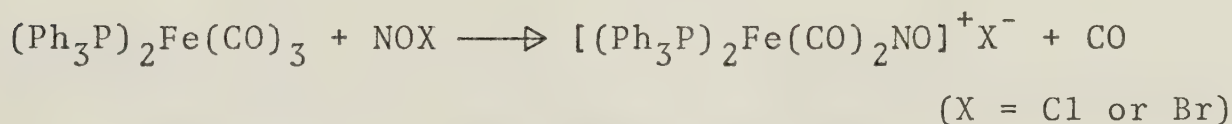
<sup>a</sup> Measured in nitrobenzene



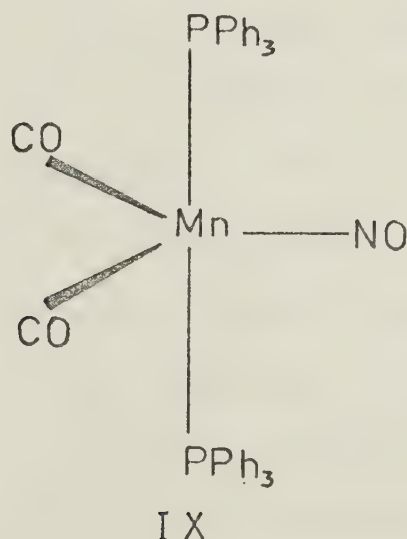
## CHAPTER II

REACTIONS OF THE NITROSONIUM CATION WITH  
BISPHOSPHINE TRICARBONYL IRONIntroduction

The isolation of a bisphosphine iron dicarbonyl nitrosyl cation was first recorded by Crooks and Johnson<sup>20</sup> in 1968. The method of preparation involved treatment of bistrisphenylphosphine tricarbonyl iron either with a nitrosyl halide or dinitrogen tetroxide, giving ready displacement



of carbon monoxide and formation of the complex nitrosyl salt. On the basis of infrared evidence, the cation was assumed to be isostructural with the isoelectronic compound  $(\text{Ph}_3\text{P})_2\text{Mn}(\text{CO})_2\text{NO}$ , (IX).<sup>21</sup>





More recently, it has been found that replacement of a transition metal bonded carbonyl group with a nitrosonium one can occur directly through use of a suitable nitrosonium salt<sup>22,23</sup> such as  $\text{NO}^+\text{BF}_4^-$  or  $\text{NO}^+\text{PF}_6^-$ .

In this work, the reaction of nitrosonium hexafluorophosphate with bistriphenylphosphine tricarbonyl iron was studied, and also with other bisphosphine derivatives in which the phosphine is "asymmetric"<sup>24</sup> (e.g.,  $\text{MePh}_2\text{P}$ ) in an attempt to clarify the probable structure of these cations using nmr techniques.

### Discussion

Preparation of bistriphenylphosphine iron dicarbonyl nitrosyl cation from the neutral tricarbonyl and dinitrogen tetroxide or nitrosyl halide, has been found to give the desired product in only approximately 50% yield.<sup>20</sup>

Using nitrosonium hexafluorophosphate as the source of  $\text{NO}^+$ , the yield may be improved to 68%, with the added advantage that the reaction goes readily at room temperature. Although acetonitrile is normally used as the solvent in this type of reaction, due to the rapid decomposition of the nitrosonium cation in other media, it has been found in this case, that the reaction proceeds equally well in chloroform. Presumably the rate of attack of the nitrosonium ion on the substrate far outweighs its own rate of decomposition. The use of chloroform also precludes the formation of





products in which the carbonyl ligand is replaced by co-ordinating solvent, as has been found for acetonitrile.<sup>22,23</sup>

Analagous treatment of bis(methyldiphenylphosphine)- and bis(dimethylphenylphosphine) tricarbonyl iron was found to result in considerably different products.

With bis(methyldiphenylphosphine) compound, the main product was found to be neutral bis(methyldiphenylphosphine)-dinitrosyl iron,  $(\text{MePh}_2\text{P})_2\text{Fe}(\text{NO})_2$ , exhibiting only two nitrosyl stretching frequencies in the infrared spectrum. This compound was fairly stable in the solid state, although its solutions decomposed slowly in air.

With bis(dimethylphenylphosphine)tricarbonyl iron, the major product was again the bisphosphine dinitrosyl derivative. This was found to be considerably less stable than the methyldiphenylphosphine analogue, especially in solution.

Okamoto has shown<sup>23</sup> that treatment of iron pentacarbonyl with nitrosonium hexafluorophosphate yields solely the moisture-sensitive salt ferrous hexafluorophosphate. It would thus appear that the substitution of a carbonyl by a phosphine in the  $\text{Fe}(\text{CO})_5$  moiety promotes the formation of stable nitrosyl complexes, possibly through two general effects. The first of these is the strengthening of the metal-carbon monoxide bond due to the weaker  $\pi$ -accepting ability of the phosphine relative to that of carbon monoxide.<sup>25</sup> This might be expected to inhibit the loss of a large number of carbonyl ligands in the molecule,



effectively limiting the amount of substitution which could occur.

The second is primarily an electronic effect. The basicity of the central metal atom in the phosphine complexes is higher, again mainly due to the weaker  $\pi$ -accepting ability of the phosphines. This too should favour the formation of a nitrosyl compound, since the better  $\pi$ -accepting ability of nitric oxide relative to carbon monoxide<sup>25</sup> could result in some removal of the "excess" electron density localised on the metal. A secondary effect of this would also be an increase in the rate of formation of a nitrosyl complex, assuming the rate determining step to be electrophilic attack of the nitrosonium ion on the metal carbonyl.

It is also of interest to note that in none of the cases considered was a product isolated in which substitution of a co-ordinated phosphine, rather than carbonyl, had occurred. Presumably the more strongly  $\sigma$ -bonded phosphine<sup>26</sup> is generally less susceptible to ejection from the molecule.

The apparently anomalous product from the reaction of bis(triphenylphosphine) tricarbonyl iron and nitrosonium ion, compared with the other phosphine derivatives, is worthy of comment. It is difficult to ascribe the preferential formation of a five co-ordinate mononitrosyl cation rather than a four co-ordinate bisphosphine dinitrosyl solely to



the stereochemical requirements of the triphenylphosphine ligand, since the latter compound may be readily prepared as a stable solid from dicarbonyl dinitrosyl iron.<sup>27</sup> Similarly, the combined effects of variation in basicity<sup>28</sup> and  $\pi$ -accepting ability<sup>25</sup> of the phosphines, ( $\text{Ph}_3\text{P}$ ,  $\text{MePh}_2\text{P}$  and  $\text{Me}_2\text{PhP}$ ) appear to cause insufficient variation in the carbonyl infrared active stretching modes (Table VI) of the bisphosphine iron tricarbonyls to assume that the metal-carbon bond order in any of these compounds is appreciably different. Thus the triphenylphosphine derivative might be again expected to follow the same reaction pathway as its congeners. A possible explanation is that the attack of  $\text{NO}^+$  on the tricarbonyl proceeds via a  $\text{S}_\text{N}2$  mechanism, involving a six co-ordinate transition state or intermediate. The steric requirements of this could perhaps be the determining factor in the reaction pathway. Obviously a rigorous kinetic investigation of these reactions is required. It is also worth noting that iron pentacarbonyl has been found to react with nitrosyl chloride to give dicarbonyl dinitrosyl iron,<sup>29</sup> in contrast with Okamoto's findings with the nitrosonium cation. This however might be due to the weaker oxidising ability of the chloride.

The infrared data for these compounds is of interest. For the product  $[(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$ , the positions of the carbonyl and nitrosyl stretching modes are consistent with those observed by Crooks and Johnson<sup>20</sup> (Table VI).

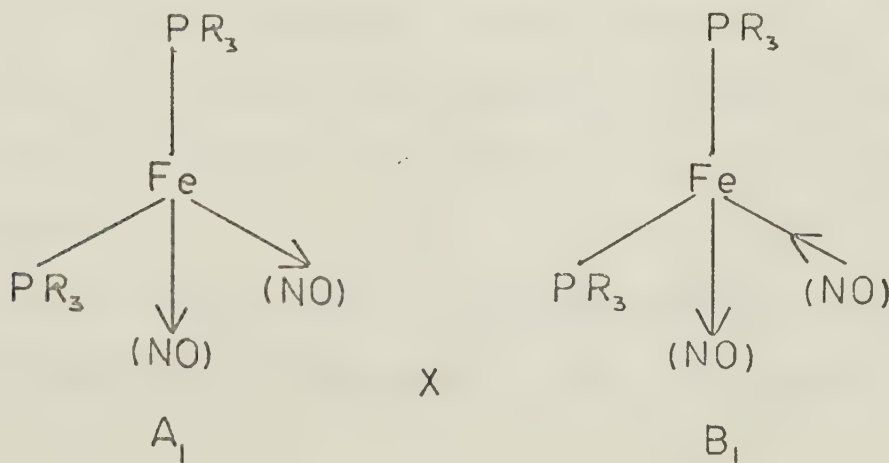




It is therefore almost certain that either method of preparation yields the same product. As expected, the bisphosphine dinitrosyl compounds exhibit two ir active nitrosyl stretching frequencies, as predicted from group theory for a structure of  $C_{2v}$  symmetry, involving tetrahedral or slightly distorted tetrahedral co-ordination about the central iron atom.<sup>30</sup> The positions of either nitrosyl band in the spectra, compared with those of similar compounds also indicate the general order of  $\pi$ -accepting ability of phosphines<sup>25</sup> to be again upheld.

<u>Compound</u>	<u><math>\nu_{NO}</math>, <math>cm^{-1}</math></u>	<u>Solvent</u>	<u>Reference</u>
$Fe(CO)_2(NO)_2$	1810, 1756	Cyclohex.	31
$Fe(Ph_3P)_2(NO)_2$	1724, 1678	$Cl_2C=CCl_2$	31
$Fe(Ph_2Me)_2(NO)_2$	1707, 1660	$CH_2Cl_2$	This work
$Fe(PhMe_2)_2(NO)_2$	1705, 1653	$CH_2Cl_2$	This work

The intensities of the two bands for the compounds prepared in this work have been found to be in the ratio 6.4:10 (high frequency band:low frequency band). Assuming  $C_{2v}$  symmetry (ir bands =  $1A_1 + 1B_1$ ) then the postulate that





the intensity of a vibrational absorption should be proportional to the square of the vector sum of the local dipoles<sup>32</sup> would place the  $A_1$  mode at higher frequency, (X).

### Nmr Spectra

The nmr spectra of the compounds prepared are of special interest, due to the form of spectral system which they represent, i.e.,  $X_nAA'X'_n$ , where  $A = {}^{31}\text{P}$  and  $X = {}^1\text{H}$ . Although systems of this type are fairly common, some having been individually treated at length,<sup>33</sup> a more general approach<sup>34</sup> has shown that in the X region of the spectrum, a doublet of separation  $N = |J_{AX} + J_{AX'}|$  and n sets of four lines symmetrical about the centre of the X pattern should arise for  $J_{XX'} = 0$ . Half of the total intensity of the spectrum should then lie in the unique doublet, with the rest shared among the n sets of lines. Despite their apparently complex nature, the spectra may however simplify to one of two extremes; namely, when  $|J_{AA'}| \gg |J_{AX} - J_{AX'}|$  the X region is reduced to a 1:2:1 triplet, typical of  $A_2X_{2n}$  spectra, or alternatively, when  $J_{AA'}$  tends to zero, to a two doublet resonance signal typical of  $X_nAM$  spectra. Of these cases, known as "deceptively simple" spectra<sup>35</sup>, at least one has been found to arise for the systems under consideration.

For both bis(methyldiphenylphosphine)- and bis(phenyldimethyl phosphine tricarbonyl iron, the methyl proton



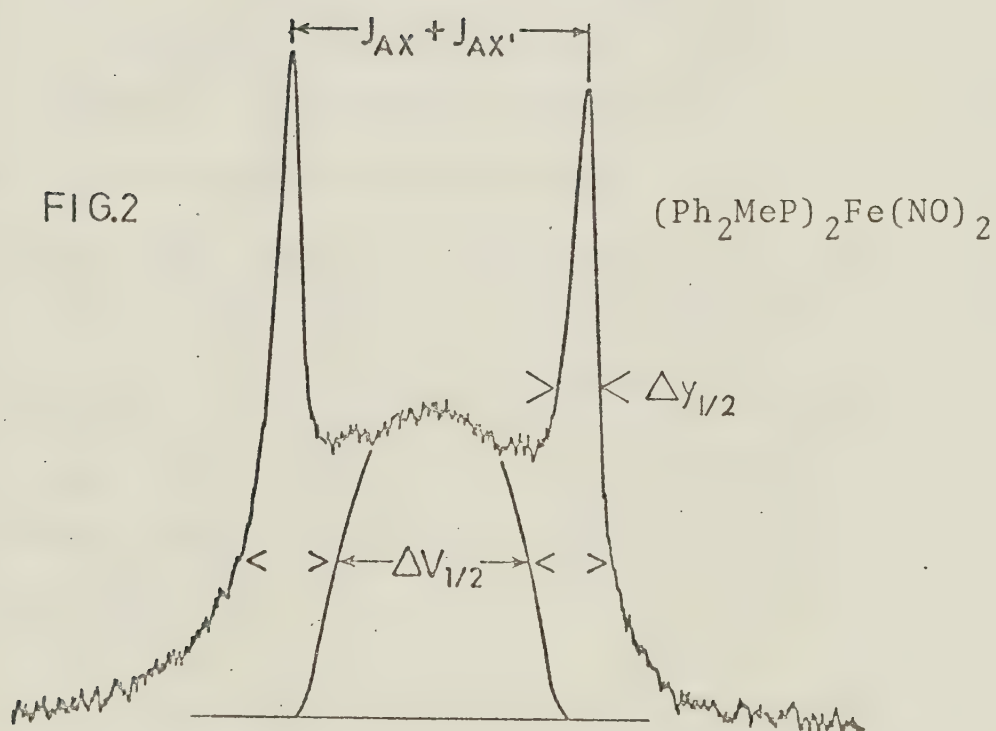
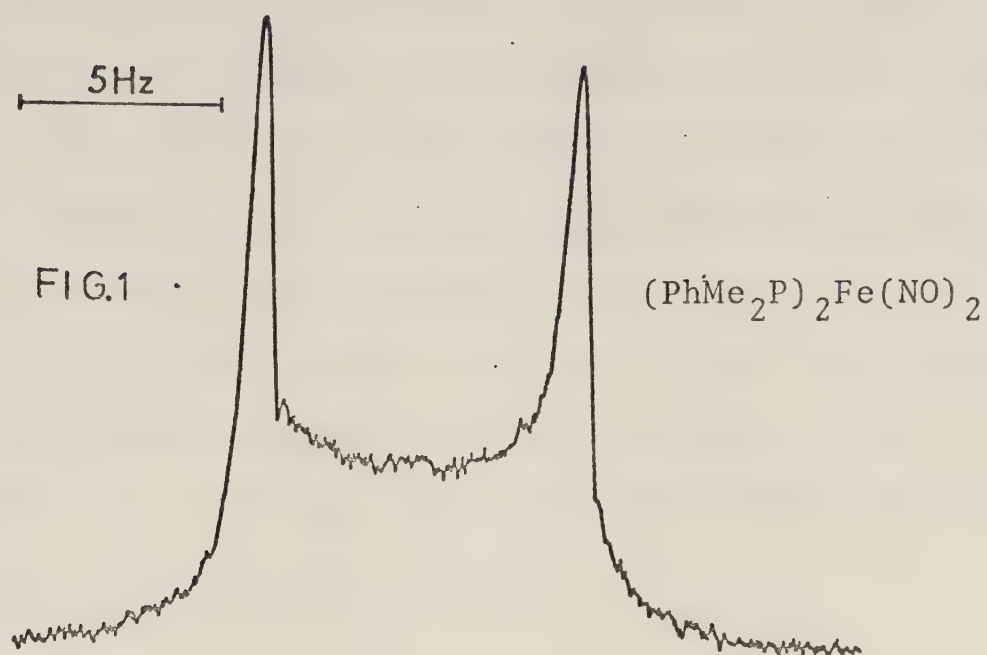
resonances appeared as 1:1 doublets of 3.5 Hz separation. If, by analogy with other known bisphosphine tricarbonyl derivatives, these compounds are assumed to have the phosphine ligands occupying the axial positions of a trigonal bipyramidal configuration (i.e. trans to one another), then fairly strong virtual coupling between the phosphorous nuclei might be expected, giving rise to a deceptively simple 1:2:1 triplet in the methyl region, or a pattern of somewhat similar character.<sup>36-39</sup> The fact that a doublet only is observed would indicate  $J_{AA'}$ , to be in actuality very close to zero. The downfield shifts of the methyl resonances relative to those of the free phosphines (Table VII) reflect an increase in the effective positive charge on the phosphorous nuclei. At the same time, the increase in  $^{31}\text{P}$ - $^1\text{H}$  coupling indicates a growth in 's' character of the P-CH bonds,<sup>40</sup> although the magnitude of the increase is less than that predicted.<sup>36</sup>

The proton spectra of the bisphosphine dinitrosyl iron compounds both exhibit a triplet pattern in the methyl region. The central peak of this was broad in each case and could not be resolved.

For bis(phenyldimethylphosphine) dinitrosyl iron an  $X_6AA'X_6'$  system, the ratio of central peak height to the average height of the outer doublet (Fig. 1) was only 1:3.24 rather than 2:1. This may be attributed to a fairly small difference in the values of  $|J_{AA'}|$  and  $|J_{AX} - J_{AX'}|$  rather







60 MHz. Nmr Spectra of  $X_n\text{AA}'X'_n$  Systems ( $n = 3$ , or  $6$ )



than the large separation required for either of the uniquely deceptively simple spectra mentioned above. The information obtainable from this spectrum is therefore limited to determination of  $|J_{AX} + J_{AX'}|$  from the separation of the doublet, and assignment of an upper limit to  $|J_{AX} - J_{AX'}|^2 / |J_{AA'}|$ . Harris has shown<sup>41</sup> that for  $X_6AA'X'_6$  systems, the absence of fine structure requires that 
$$\frac{|J_{AX} - J_{AX'}|^2}{2|J_{AA'}|} < 0.5 \Delta\nu_{\frac{1}{2}},$$
 where  $\Delta\nu_{\frac{1}{2}}$  is the width at half height of the central resonance line. From this,  $|J_{AX} - J_{AX'}|^2 / |J_{AA'}|$  may be estimated to be less than 9.8 Hz. A closer estimate of the true value can be obtained from a comparison of the ratio of the central and outer resonance peak heights, using the method of Finer and Harris<sup>41</sup> (Appendix). Unfortunately this depends mainly on the value  $\Delta\nu_{\frac{1}{2}}$ , which cannot be determined accurately.

For bis(methyldiphenylphosphine) dinitrosyl iron, an  $X_3AA'X'_3$  system, the ratio of peak heights for the triplet was 2.06:1:2.06. The condition for no resolution of the central envelope is approximately the same as above, thus requiring  $|J_{AX} - J_{AX'}|^2 / |J_{AA'}|$  to be less than 9.3 Hz. Again a better estimate may be obtained from peak height measurements (Fig. 2).



## EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Solvents were dried as described previously. Acetonitrile, decahydronaphthalene (decalin), n-octane and diethyl ether were used as obtained from commercial sources. Nitrosonium hexafluorophosphate was used as supplied by the Ozark-Mahoning Company. Chromatography was carried out on neutral alumina (BDH, Brockman, activity II).

Microanalyses, infrared and nmr spectra, were obtained from the sources previously mentioned.

Preparation of  $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ 

The starting material  $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$  was prepared from iron pentacarbonyl and triphenylphosphine by literature methods.<sup>42</sup>

Preparation of  $(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{CO})_3$  and  $(\text{PhMe}_2\text{P})_2\text{Fe}(\text{CO})_3$ 

Typically, an excess of phosphine (50 mmole) was added to iron pentacarbonyl (22.9 mmole) in decahydronaphthalene (150 ml) and the mixture kept at 120°C for 22 hrs, while rapidly magnetically stirred. After cooling to room temperature, the solution was filtered through a medium pore sinter and the filtrate cooled to approximately -10°C in an ice-salt bath. Pale yellow crystals formed fairly rapidly. These were filtered off, recrystallised





from methylene chloride/n-hexane, washed once with cold n-pentane (0°C, 20 ml) and dried in high vacuum (0.2mm, 2 hrs). The reaction was found to proceed equally well in refluxing n-octane, rather than decahydronaphthalene.

Preparation of  $[(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$

Nitrosonium hexafluorophosphate (0.08 gm, 0.46 mmole) was added as a solid to  $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$  (0.3 gm, 0.45 mmole) in acetonitrile (20 ml) and the solution magnetically stirred until all gas evolution had ceased (approx. 10 mins). The solution was filtered and the product precipitated by the addition of diethyl ether (10 ml). The yellow micro-crystalline solid formed was filtered off, washed with diethyl ether (3 x 3 ml) and dried under vacuum (0.2 mm, 2 hrs). Using chloroform as solvent instead of acetonitrile gave the same product in almost identical yield.

Preparation of  $(\text{PhMe}_2\text{P})_2\text{Fe}(\text{NO})_2$  and  $(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{NO})_2$

A sample of nitrosonium hexafluorophosphate (0.42 gm, 2.4 mmole) in acetonitrile (7 ml) was slowly added to  $(\text{PhMe}_2\text{P})_2\text{Fe}(\text{CO})_3$  (1 gm, 2.4 mmole) in acetonitrile (10 ml). The mixture was magnetically stirred until all gas evolution had ceased (approx, 10 mins). After filtering, solvent was removed on a rotary evaporator, and the red oily residue chromatographed in methylene chloride on an alumina column (23 cm x 2.4 cm). The product eluted as a red band in



methylene chloride, followed by starting material. Recrystallisation from n-hexane afforded the dinitrosyl as dark red crystals.

Similar treatment of  $(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{CO})_3$  (1.08 gm, 2.0 mmole) with  $\text{NO}^+\text{PF}_6^-$  (0.36 gm, 2.0 mmole) gave the analogous dinitrosyl as fine wine-red crystals.



TABLE V

Analytical Data and Physical Properties

Compound	Calculated %			Found %			% Yield	Colour	MP
	C	H	N	C	H	N			
$[(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$	56.24	3.72	1.72	56.06	3.71	1.85	68.2	Yellow	dec. 170-175
$(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{CO})_3$	64.46	4.85	-	64.04	4.85	-	60.4	Lemon	168-170
$(\text{PhMe}_2\text{P})_2\text{Fe}(\text{CO})_3$	54.83	5.32	-	54.91	5.42	-	58.6	Colour-less	76-78
$(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{NO})_2$	60.48	5.08	5.43	59.84	5.10	5.29	17.1 <sup>a</sup>	Wine-red	138-140
$(\text{PhMe}_2\text{P})_2\text{Fe}(\text{NO})_2$	49.00	5.65	7.14	49.56	5.67	7.32	24.0 <sup>a</sup>	Dark red	66-68

<sup>a</sup> Yield based on bisphosphine tricarbonyl iron (starting material).





TABLE VI

Infrared Data<sup>a</sup>

Compound	$\nu_{\text{CO}}$ $\text{cm}^{-1}$	$\nu_{\text{NO}}$ $\text{cm}^{-1}$	Solvent
$[(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$	2051, 1992	1789	Acetonitrile
$(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{CO})_3$	1886	-	<u>n</u> -Hexane
$(\text{PhMe}_2\text{P})_2\text{Fe}(\text{CO})_3$	1883	-	<u>n</u> -Hexane
$(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{NO})_2$	-	1707, 1660	Methylene chloride
$(\text{PhMe}_2\text{P})_2\text{Fe}(\text{NO})_2$	-	1701, 1653	Methylene chloride

<sup>a</sup> Measured in 0.5 mm KBr disc cells.



TABLE VII

 $^1\text{H}$  Nmr Spectral Data

Compound	Solvent	$\tau_{\text{C}_6\text{H}_5}^{\text{a}}$	$\tau_{\text{CH}_3}^{\text{b}}$	$ J_{\text{AX}} + J_{\text{AX}} $	Upper limit	Cal. limit
					$ J_{\text{AX}} - J_{\text{AX}} ^2$	$ J_{\text{AX}} - J_{\text{AX}} ^2$
					$ J_{\text{AA}} $	$ J_{\text{AA}} $
$\text{Ph}_2\text{MeP}$	$\text{CDCl}_3$	2.71	8.44, 8.50	3.0 <sup>c</sup>	-	-
$\text{PhMe}_2\text{P}$	$\text{CDCl}_3$	2.75	8.73, 8.78	2.8 <sup>c</sup>	-	-
$[(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_2\text{NO}]^+ \text{PF}_6^-$	$\text{CD}_2\text{Cl}_2$	2.23	-	-	-	-
$(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{CO})_3$	$\text{CD}_2\text{Cl}_2$	2.37, 2.59	7.78, 7.89	3.5	-	-
$(\text{PhMe}_2\text{P})_2\text{Fe}(\text{CO})_3$	$\text{CD}_2\text{Cl}_2$	2.24, 2.58	8.06, 8.18	3.5	-	-
$(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{NO})_2$	$\text{CDCl}_3$	2, 36	8.23, 8.35	7.4	9.3	2.68
$(\text{PhMe}_2\text{P})_2\text{Fe}(\text{NO})_2$	$\text{CDCl}_3$	2.32, 2.38	8.17, 8.30	8.0	9.8	3.34

<sup>a</sup> Refers to main resonances of complex pattern.<sup>b</sup> Positions of arms of doublet.<sup>c</sup> In this case  $|J_{\text{AX}}| = 0$ .



# CHAPTER III

## ARYLAZO DERIVATIVES OF BISPHOSPHINE TRICARBONYL IRON AND RELATED COMPOUNDS

### Introduction

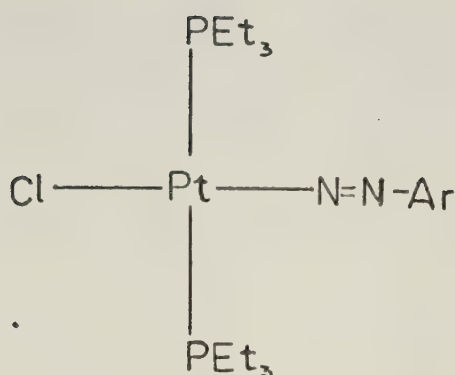
The search for a transition metal system capable of converting gaseous nitrogen to ammonia under relatively mild conditions has, in recent years, stimulated research into the chemistry of metal co-ordinated nitrogen complexes.

The first compound of a transition metal containing the nitrogen molecule as a neutral ligand was prepared by Allen and Senoff<sup>43</sup> in 1965. Treatment of this complex  $[\text{Ru}^{(\text{II})}(\text{NH}_3)_2\text{N}_2]\text{X}_2$ , ( $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{BF}_4^-, \text{PF}_6^-$ ) with sodium borohydride was initially found to produce sufficient ammonia to indicate that at least half a mole of co-ordinated nitrogen was being reduced per mole of complex. However, recent work has shown that reduction of co-ordinated nitrogen to ammonia does not in fact take place.<sup>44</sup>

More recently, Parshall has shown<sup>45</sup> that a complex platinum hydride can convert bound nitrogen to ammonia in the presence of hydrogen, using an aryldiazonium salt as the model for a metal-nitrogen system. One of the products of this investigation,  $\text{ArN}_2\text{Pt}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2\text{Cl}$ , (XI)

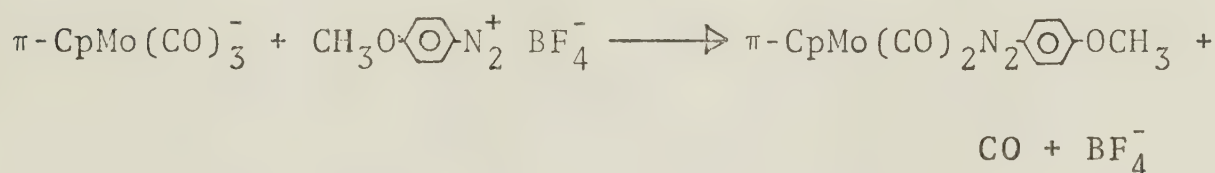






XI

has in many respects been found to resemble the neutral aryl-azo carbonyl compounds of molybdenum, prepared by King and Bisnette,<sup>46,47</sup> through reaction of  $\pi$ -cyclopentadiene molybdenum tricarbonyl anion and an aryldiazonium fluoroborate.

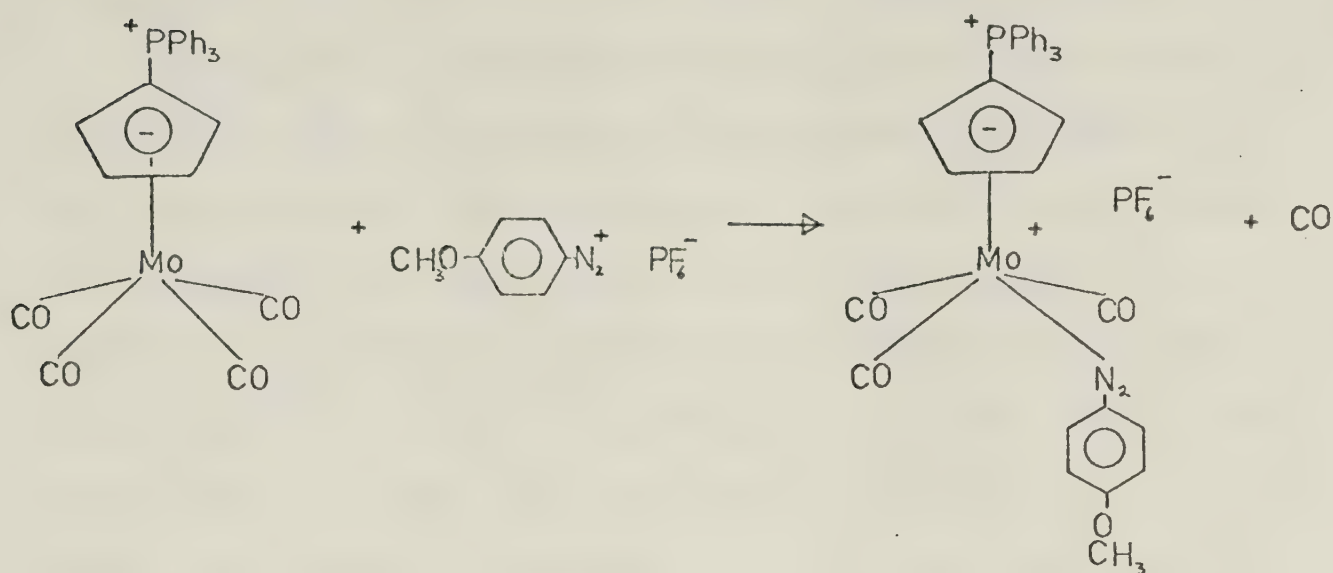


King<sup>47</sup> initially proposed that formation of this type of complex was unique to that anion. However it has since been shown that  $\pi$ -cyclopentadiene tungsten tricarbonyl anion,<sup>48</sup> as well as several more complex anions of molybdenum,<sup>49,50</sup> can react in the same manner to produce neutral compounds with loss of one carbonyl group per arylazo group introduced. Only one anomalous reaction with an organometallic anion has so far been recorded.<sup>51</sup>

One of the earliest reactions of a neutral Lewis base with an aryldiazonium salt was noted by Cashman and Lalor,<sup>13</sup> who prepared p-anisylazo triphenylphosphonium  $\pi$ -cyclopentadienylide molybdenum dicarbonyl hexafluoro-



phosphate from Cpylid  $\text{Mo(CO)}_3$  (isoelectronic with  $\pi\text{-CpMo(CO)}_3^-$ ) and the parent diazonium salt, (XII).



XII

In terms of base strength, Cpylid  $\text{Mo(CO)}_3$  may be regarded as a weaker base than  $\pi\text{-CpMo(CO)}_3^-$ ,<sup>52</sup> towards protonation, and a slightly better base, if not a better nucleophile than bistrisphenylphosphine tricarbonyl iron.<sup>5,10</sup>

However, in view of the similarity of Cpylid  $\text{Mo(CO)}_3$  to the latter compound, especially with respect to the formation of adducts,<sup>18</sup> it was decided to investigate the reactions of bistrisphenylphosphine tricarbonyl iron and related derivatives with aryldiazonium salts.

### Discussion

The bisphosphine arylazo iron dicarbonyl cations described, were isolated as stable orange-red solids that

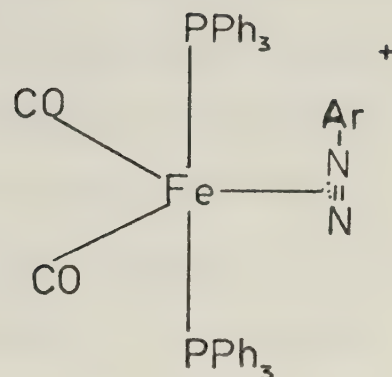
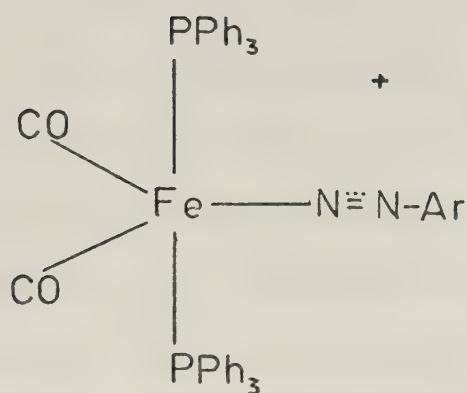


were thermally stable and not oxidized by air. Soluble in the more polar organic solvents, they gave solutions which decomposed only slowly in air, over a period of hours.

In general, the compounds were prepared by first mixing the solid bisphosphine tricarbonyl iron and solid aryldiazonium salt (the fluoroborate because of high stability) together and then adding methylene chloride to the mixture under nitrogen. Immediate gas evolution occurred, ceasing after a period of minutes or sometimes hours. The orange-red solutions obtained could be purified by chromatography and recrystallisation to give the desired products in fair yield.

The infrared spectra of all of the compounds obtained exhibited only two strong metal carbonyl stretching frequencies in methylene chloride, similar in position and intensity to those of the isoelectronic bistriphenylphosphine iron dicarbonyl nitrosyl cation.<sup>20</sup> In view of this, the structure of all compounds prepared has been tentatively assigned as that based on a trigonal bipyramidal configuration about the iron atom, the phosphines occupying the axial positions and the arylazo group one of the equatorial ones, (XIII). It has been assumed that the arylazo group co-ordinates in an end on (XIII) rather than side on fashion (XIV) to the transition metal, in analogy to CO, NO<sup>+</sup>, CN<sup>-</sup>, and RNC (R = aryl or alkyl) with which it is isoelectronic.<sup>53</sup>





The bonding of the arylazo group in these compounds may be rationalised in terms of a derivative of a molecular nitrogen complex. For free nitrogen, lone electron pairs localised on each nitrogen atom may account for the formation of a  $\sigma$ -bond to the transition metal via one end of the  $N_2$  molecule, whereas back donation of  $\pi$ -electron density from the metal into an empty antibonding molecular orbital of the  $N_2$  ligand would give rise to  $\pi$ -bond formation.<sup>54</sup> The arylazo group may therefore be regarded as the product of lone-pair coordination by that nitrogen atom not bonded to the transition metal, to an aryl carbonium ion. Collman has contended<sup>55</sup> that  $N_2$  is a stronger  $\pi$ -acid than CO, similar to  $NO^+$  in that both are strong  $\pi$ -acids and weak  $\sigma$ -donors. This view has been somewhat reinforced by comparative molecular orbital calculations for the two ligands.<sup>54</sup>

The co-ordination of an aryl carbonium ion to one end of the  $N_2$  molecule might be expected to alter the bonding properties of the ligand in two ways. Firstly, if the

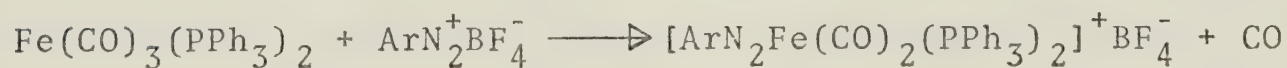
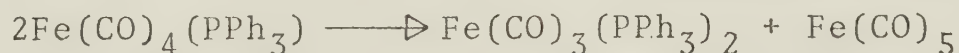




N-aryl bond is assumed to be a simple  $\sigma$  one, then withdrawal of  $\sigma$ -electron density from the molecule could be communicated to the metal-nitrogen  $\sigma$ -bond, resulting in a slight bond weakening. Secondly, the charge on the ligand might be expected to increase its electron-accepting ability, thus increasing the strength of the metal-ligand  $\pi$ -bond while weakening the metal-nitrogen  $\sigma$  one.

It is therefore suggested that in comparison with  $N_2$ , the arylazo ligand may be regarded as a weaker  $\sigma$ -donor and stronger  $\pi$ -acid. Exactly how the ligand compares with the nitrosonium ion is difficult to say. However, if the carbonyl stretching frequencies of  $[(Ph_3P)_2Fe(CO)_2NO]^+PF_6^-$  ( $\nu = 2051, 1992\text{ cm}^{-1}$ ) and a typical diazonium derivative  $[(Ph_3P)_2Fe(CO)_2N_2Ph]^+BF_4^-$  ( $\nu = 2030, 1973\text{ cm}^{-1}$ ) are considered, it would appear that the arylazo group is, if anything, a slightly weaker  $\pi$ -acceptor than NO, in this type of compound.

The two ligands have some chemical similarities; for example the aryldiazonium salt will react with triphenylphosphine tetracarbonyl iron to give a bisphosphine complex, does  $NO^{+20}$  However, it has in general been found that few



of the reactions of the nitrosonium cation can be duplicated by the arylazo group. Thus no reaction occurs with the



Group VI metal hexacarbonyls, benzenechromium tricarbonyl,  $\pi$ -cyclopentadienylmanganese tricarbonyl, or the more common metal-metal bonded carbonyl dimers. One of the limiting factors in these reactions is the absence of a suitable solvent for the aryldiazonium salt. Where reaction occurs rapidly, as with the bisphosphine tricarbonyl iron compounds, the choice of solvent is not too critical, since it appears that the reaction rate far exceeds that of decomposition of the diazonium salt. However, where a reaction might possibly proceed at a slightly elevated temperature, decomposition of the diazonium salt, even in acetone, is quite rapid. Similar instability with respect to ultra-violet irradiation has also been noted, nitrogen loss accompanying



decomposition.<sup>56</sup> Of even more importance are the relative electrophilicities of the two cations. With respect to the rate of reaction with bistrisphenylphosphine tricarbonyl iron, observation would place  $\text{NO}^+$  as the better electrophile, assuming similar reaction mechanisms. It would therefore appear that reactions of aryl diazonium salts and organometallic compounds would be more likely to occur with those neutral complexes which may be regarded as strong neutral Lewis bases (i.e., undergo ready protonation, easily form adducts with mercuric halides, etc.). However,

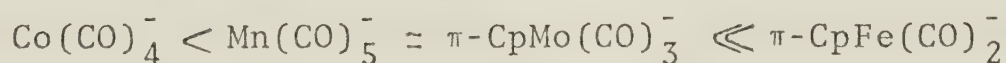


results obtained from the reactions of simple organometallic anions and aryldiazonium salts are conflicting.

If the nucleophilicities of the more common anions are compared relative to  $\text{Co}(\text{CO})_4^-$ <sup>57,58</sup>

<u>Anion</u>	<u>Relative Nucleophilicity</u>
$\text{CpFe}(\text{CO})_2^-$	70,000,000
$\text{CpRu}(\text{CO})_2^-$	7,500,000
$\text{CpNi}(\text{CO})^-$	5,500,000
$\text{Re}(\text{CO})_5^-$	25,000
$\text{CpW}(\text{CO})_3^-$	500
$\text{Mn}(\text{CO})_5^-$	77
$\text{CpMo}(\text{CO})_3^-$	67
$\text{CpCr}(\text{CO})_3^-$	4
$\text{Co}(\text{CO})_4^-$	1

it would appear that  $\pi\text{-CpMo}(\text{CO})_3^-$  and  $\pi\text{-CpW}(\text{CO})_3^-$  (both of which react with aryldiazonium salts<sup>46,47,48</sup>) may be regarded as only weak nucleophiles, of strengths comparable to  $\text{Mn}(\text{CO})_5^-$  and  $\text{Co}(\text{CO})_4^-$ . This is in accord with the findings of Okamoto<sup>23</sup>, who showed the reaction of these ions with the nitrosonium cation to generate an order of increasing nucleophilicity given as:



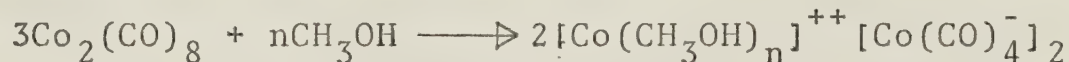
Thus it might be expected that both  $\text{Co}(\text{CO})_4^-$  and  $\text{Mn}(\text{CO})_5^-$





could be made to react with an aryldiazonium salt, contrary to the findings of King.<sup>47</sup>

Treatment of a number of aryldiazonium salts with the  $\text{Co}(\text{CO})_4^-$  ion (prepared by sodium amalgam reduction of the parent dimer in tetrahydrofuran) at both room temperature and  $-60^\circ\text{C}$  was found to yield a mixture of dicobalt octacarbonyl and bis(cobalt tetracarbonyl) mercury. In each case rapid gas evolution occurred upon addition of the diazonium salt, followed by a colour change from grey to reddish-brown. Allowing a diazonium salt to stand in tetrahydrofuran over free mercury did not appear to alter appreciably its slow rate of decomposition. Preparation and reaction of the  $\text{Co}(\text{CO})_4^-$  ion, in methanol,<sup>59</sup> at  $0^\circ\text{C}$



was likewise found to give a mixture of  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_4(\text{CO})_{12}$  identified by their infrared spectra. Similar treatment of the  $\text{Mn}(\text{CO})_5^-$  ion regenerated the dimer  $\text{Mn}_2(\text{CO})_{10}$ , while  $\text{V}(\text{CO})_6^-$  was simply oxidised to  $\text{V}(\text{CO})_6$ .

It is therefore indicated that factors other than the nucleophilicity of the anion are of consequence in reactions with aryldiazonium salts. One of these is the co-ordination number of the central metal atom of the organometallic ion. It has been shown<sup>60</sup> that for a given electronic configuration, the most favoured co-ordination number is six. Thus substitution of a carbonyl by an arylazo group might



possibly be expected to occur more readily for those ions of that particular co-ordination number. The size of the central metal atom is also of importance. A comparison of the ions  $\text{Mn}(\text{CO})_5^-$ ,  $\text{Re}(\text{CO})_5^-$  and  $\pi\text{-CpM}(\text{CO})_3^-$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) would indicate an increase in nucleophilicity with increasing metal atom size, in each series. At the same time, the larger d orbitals associated with the larger metal atoms could stabilise formation of compounds with  $\pi$ -acids such as the arylazo ligand. Hence the formation of such compounds by  $\pi\text{-CpMo}(\text{CO})_3^-$  and  $\pi\text{-CpW}(\text{CO})_3^-$  might be attributable to the fact that they are of a favourable co-ordination number ("5.5"),<sup>61</sup> are medium strength nucleophiles, if not bases, and with central metal atoms sufficiently large enough for good d-back-bonding to co-ordinating ligands. Where such favourable conditions are not met, it is possible that the ion is either oxidised by the diazonium salt (e.g.  $\text{V}(\text{CO})_6^-$ ), or forms an unstable neutral arylazo derivative, which subsequently decomposes to give products other than those expected for simple oxidation. This could perhaps be the case for the  $\text{Co}(\text{CO})_4^-$  ion.

### Infrared Spectra

The infrared spectra of the prepared compounds are in agreement with a structure similar to the bisphosphine dicarbonyl nitrosyl iron cation mentioned previously.

Group theory would predict two ir active carbonyl stretching modes ( $1A_1 + 1B_1$ ) for a structure of  $C_{2v}$  symmetry,



both of which are observed. The positions of the carbonyl bands do not appear to be appreciably susceptible to the changes in electron withdrawing or donating ability of the substituent on the phenyl ring of the arylazo group, nor to changes in position on the ring of any one substituent. Attempts to correlate band positions to Hammet-Taft parameters<sup>62</sup> have been unsuccessful, although it is worth noting that all of the nitro substituted compounds prepared do exhibit quite higher carbonyl stretching frequencies than other derivatives. (The nitro group is a notably deactivating phenyl group substituent, having large Hammet-Taft parameters). This might be ascribed to a greater withdrawal of electron density from the central iron atom in the nitro phenyl azo compounds, resulting in less  $\pi$ -back-bonding to the carbonyls and a corresponding increase in C-O bond order and stretching frequency.

The N-N vibrations in these compounds have been identified by  $^{15}\text{N}$  substitution. Previously, Parshall had shown<sup>45</sup> the N-N stretching frequencies in  $\pi\text{-CpMo(CO)}_2\text{N}_2\text{Ar}$  and  $\text{ArN}_2\text{Pt[P(C}_2\text{H}_5)_3]_2\text{Cl}$  to be unexpectedly low, arising in the region  $1570\text{-}1440\text{ cm}^{-1}$ . However, due to the cationic nature of the arylazo compounds prepared here, an increase in stretching frequency over these values was expected.

A comparison of the spectra of all compounds in the region  $2100\text{-}1400\text{ cm}^{-1}$  showed a common band at approximately  $1700\text{ cm}^{-1}$ , of about two-thirds the intensity of the higher





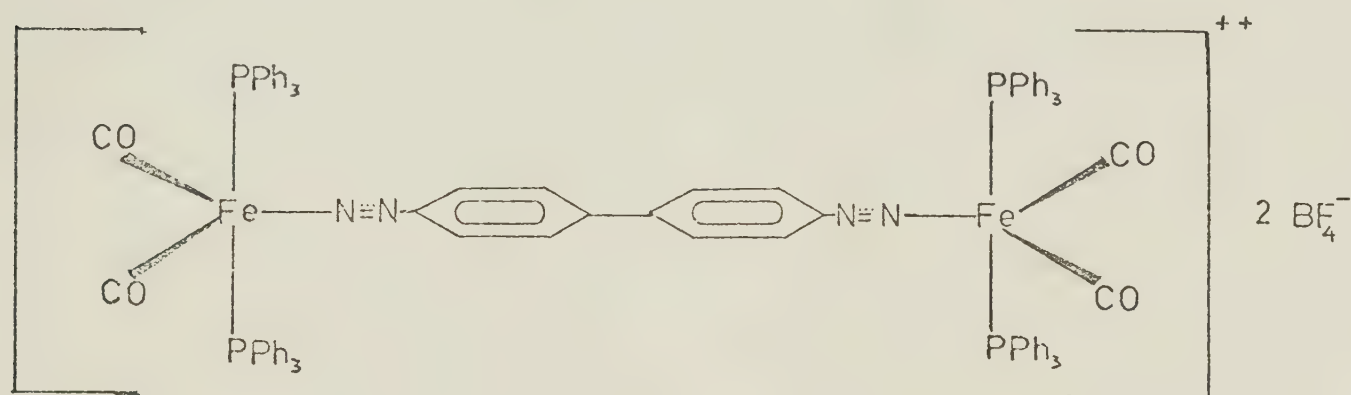
frequency carbonyl absorptions. Preparation of phenyl and p-nitrophenyl diazonium fluoborates from a sample of 95.61 atom % sodium ( $^{15}\text{N}$ ) nitrite, and then reaction to form the bisphosphine dicarbonyl iron derivatives caused this band in both cases to be lowered in frequency by  $25\text{ cm}^{-1}$ . (Mathematically predicted shift =  $28\text{ cm}^{-1}$ ). No change in carbonyl stretching frequency due to coupling was observed, within the limits of measurement, for either compound. The N-N stretching frequencies of all other derivatives have therefore been assigned to the intense bands in this region of the spectrum (Table IX). Again, the positions of the bands do not appear to have any simple dependence on the electronic properties of the phenyl ring substituents. However, it may be seen that the N-N stretch appears to show a reverse effect with substituent to that of the C-O stretch. Thus the nitro derivatives have the highest C-O frequencies but the lowest N-N frequencies. This might be expected for a strongly deactivating substituent, since loss of  $\pi$ -electron density in the phenyl ring could increase  $\pi$ -acidity in the arylazo ligand, thus increasing the amount of  $\pi$ -back-bonding from the metal, decreasing the N-N bond order and hence presumably reducing the stretching frequency. The position of the N-N absorption would certainly indicate a bond order closer to two than three. Whether this would result in a bent rather than linear metal-N-N bond remains to be seen. It has, however, been shown that for one





complex of the isoelectronic ligand methyl isocyanide,<sup>63</sup> no bending of the metal-C-N bond occurs, even though extensive  $\pi$ -back-bonding from the metal to the ligand is indicated.

The infrared spectrum of the product of the reaction between bistrisphenylphosphine tricarbonyl iron and p-diazo benzidine fluoroborate exhibits only two carbonyl and one azo stretching frequencies, similar to the monomeric arylazo derivatives prepared earlier. The simplicity of the spectrum favours a highly symmetric structure for this compound, such as that shown in XV.



Due to the similarity of the carbonyl and azo band positions in the infrared spectrum to those of the monomeric arylazo species, it is thought that the compound is best regarded as having separated unipositive charges localised on the metal atoms at each end of the molecule.

Conductivity measurements in nitrobenzene have confirmed the product to be a 1:2 electrolyte (25.5°C, 1mM, conductance = 56.2 mhos cm<sup>2</sup> moles<sup>-1</sup>).



Nmr Spectra

Assignment of the nmr spectra of these compounds is routine. Chemical shifts have been listed in Table X.



## EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Solvents were dried as described previously. Acetone was used as obtained from commercial sources.

The diazonium tetrafluoroborates of aniline,<sup>64</sup> o-, m- and p-nitroaniline;<sup>65</sup> o-, m- and p-toluidine;<sup>64</sup> p-anisidine; o-amino methyl benzoate;<sup>66</sup> and benzidine<sup>67</sup> were prepared by standard literature methods. The  $^{15}\text{N}$ -enriched diazonium tetrafluoroborates of aniline and p-nitroaniline were obtained by these methods from a sample of sodium ( $^{15}\text{N}$ ) nitrite (95.61 atom%  $^{15}\text{N}$ ), acquired from Merck, Sharp & Dohme Ltd.

Bis(triphenylphosphine) tricarbonyl iron and bis(methyldiphenyl phosphine) tricarbonyl iron were prepared as described previously.

Chromatography was carried out on neutral alumina (BDH, Brockman, activity II).

Microanalyses, infrared and nmr spectra were acquired from the same sources as before.

Preparation of bisphosphine iron dicarbonyl arylazo tetrafluoroborate

Typically, an excess of aryldiazonium tetrafluoroborate (2 mmole) was added as a solid to bis(triphenylphosphine) tricarbonyl iron (0.66 gm, 1 mmole) dissolved in methylene chloride (10 ml), with vigorous magnetic stirring. Rapid





gas evolution occurred. After stirring for two hours, the orange-red solution was filtered and chromatographed directly on an alumina column (17 x 2.4 cm) in methylene chloride/acetone (1:3 by volume). Unreacted  $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$  eluted as a yellow band, followed by the desired product as a red band, in pure acetone. Considerable gas evolution occurred on the column, either due to the boiling of solvent caused by adsorption, or to the decomposition of unreacted diazonium salt.

After reducing the volume of acetone present to a minimum on a rotary evaporator, at room temperature, methylene chloride (12 ml) was added, the solution filtered, and a small quantity of *n*-pentane further added. Cooling to 0°C afforded fine orange crystals of  $[(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_2\text{N}_2\text{Ar}]^+\text{BF}_4^-$ .

A slightly different procedure was used for the preparation of the *p*-diazobenzidine derivative. Thus an excess of bistriphenylphosphine tricarbonyl iron (0.85 gm, 1.28 mmole) was added to a sample of *p*-diazobenzidine tetrafluoroborate (0.2 gm, 0.52 mmole) in acetone (20 ml), and the solution stirred rapidly for three hours. Gas evolution occurred slowly, the solution eventually turning red. After filtering, the product was precipitated from solution by the addition of diethyl ether (100 ml) and then recrystallised from acetone/diethyl ether at -78°C as fine yellow crystals.



TABLE VIII

Analytical Data and Physical Properties

Compound	Calculated %			Found %			% Yield	Colour	MP
	C	H	N	C	H	N			
$[(C_6H_5)N_2Fe(PPh_3)_2(CO)]_2^+BF_4^-$	63.79	4.25	3.38	62.70	4.31	3.35	18.7	Pale orange	183-188
$[(p-MeOC_6H_4)N_2Fe(PPh_3)_2(CO)]_2^+BF_4^-$	62.96	4.34	3.26	61.48	4.43	2.76	12.8	Orange-yellow	177-180
$[(p-MeC_6H_4)N_2Fe(PPh_3)_2(CO)]_2^+BF_4^-$	64.16	4.42	3.32	60.43	4.42	3.00	13.1	Orange	171-175
$[(m-MeC_6H_4)N_2Fe(PPh_3)_2(CO)]_2^+BF_4^-$	64.16	4.42	3.32	64.17	4.83	3.31	10.5	Orange	170-174
$[(o-MeC_6H_4)N_2Fe(PPh_3)_2(CO)]_2^+BF_4^-$	64.16	4.42	3.32	62.76	4.83	3.36	8.2	Orange	183-195
$[(p-NO_2C_6H_4)N_2Fe(PPh_3)_2(CO)]_2^+BF_4^-$	60.51	3.92	4.81	59.91	4.19	4.88	23.6	Orange	157-161
$[(m-NO_2C_6H_4)N_2Fe(PPh_3)_2(CO)]_2^+BF_4^-$	60.51	3.92	4.81	59.97	4.27	4.84	32.1	Orange	164-167
$[(o-NO_2C_6H_4)N_2Fe(PPh_3)_2(CO)]_2^+BF_4^-$	60.51	3.92	4.81	60.34	4.34	4.15	20.0	Orange	161-165
$[(o-MeOCOC_6H_4)N_2Fe(PPh_3)_2(CO)]_2^+BF_4^-$	62.33	4.20	3.16	62.28	4.46	2.87	17.4	Orange	Dec. > 145

continued.....



Table VIII - (continued)

$[(o\text{-EtOCOC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2]$ $(\text{CO})_2\text{I}^+\text{BF}_4^-$	62.69	4.36	3.11	61.11	4.61	3.13	11.1	Orange	170-180
$[(p\text{-MeC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_2\text{Me})_2]$ $(\text{CO})_2\text{I}^+\text{BF}_4^-$	58.52	4.63	3.90	58.20	4.86	3.84	24.8	Orange	64-68
$p\text{-}[(\text{-C}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{I}^{++}_2$ $2\text{BF}_4^-$	63.87	4.14	3.38	63.76	4.52	3.20	32.1	Yellow	Dec. > 120



TABLE IX

Infrared Data<sup>a</sup>

Compound	$\nu_{\text{CO}}$ $\text{cm}^{-1}$	$\nu_{\text{NN}}$ $\text{cm}^{-1}$
$[\text{C}_6\text{H}_5)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2030 1973	1718
$[\text{p-MeOC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2026 1969	1723
$[\text{p-MeC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2027 1970	1723
$[\text{m-MeC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2029 1973	1725
$[\text{o-MeC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2028 1972	1729
$[\text{p-NO}_2\text{C}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2037 1982	1702
$[\text{m-NO}_2\text{C}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2036 1982	1699
$[\text{o-NO}_2\text{C}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2036 1981	1709
$[\text{o-MeOCOC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2029 1974	1720
$[\text{o-EtOCOC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2030 1973	1719
$[\text{p-MeC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_2\text{Me})_2(\text{CO})_2]\text{BF}_4^+$	2026 1967	1722
$\text{p-}[\text{(-C}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]\text{BF}_4^+$	2029 1974	1716

<sup>a</sup> Taken in methylene chloride (0.5 mm KBr disc cells).





TABLE X

 $^1\text{H}$  Nmr Spectral Data

Compound	Solvent	$\tau_{\text{C}_6\text{H}_5^a}$	$\tau_{\text{CH}_3}$
$[(\text{C}_6\text{H}_5)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	Acetone $d^6$	2.25	-
$[(p\text{-MeOC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	$\text{CD}_2\text{Cl}_2$	2.37 3.56	6.19
$[(p\text{-MeC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	Acetone $d^6$	2.40 3.00, 3.54	7.68
$[(m\text{-MeC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	Acetone $d^6$	2.35 2.86, 3.87	7.87
$[(o\text{-MeC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	$\text{CD}_2\text{Cl}_2$	2.48	8.17
$[(p\text{-NO}_2\text{C}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	$\text{CD}_2\text{Cl}_2$	2.40 3.38, 3.53	-
$[(m\text{-NO}_2\text{C}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	$\text{CD}_2\text{Cl}_2$	2.38 2.88	-
$[(o\text{-NQ}_2\text{C}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	$\text{CD}_2\text{Cl}_2$	2.40	-
$[(o\text{-MeOCOC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	Too insoluble for good spectra		
$[(o\text{-EtOCOC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{+\text{BF}_4^-}$	Too insoluble for good spectra		
$[(p\text{-MeC}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_2\text{Me})_2(\text{CO})_2]^{+\text{BF}_4^-}$	$\text{CD}_2\text{Cl}_2$	2.58 3.14, 3.58	7.79 <sup>b</sup>
$p\text{-}[(\text{-C}_6\text{H}_4)_2\text{N}_2\text{Fe}(\text{PPh}_3)_2(\text{CO})_2]^{++} 2\text{BF}_4^-$	Acetone $d^6$	3.28	-

<sup>a</sup> Paired values refer to the AA'BB' pattern of a p-substituted phenyl ring. This pattern was not completely resolved.

<sup>b</sup> Broad singlet.



## APPENDIX

## CALCULATION OF THE CENTRE HEIGHT OF THE ENVELOPE

FOR AN  $X_nAA'X'_n$  NMR SPECTRUM ( $n = 3$  or  $6$ )

Finer and Harris have shown<sup>41</sup> that for an  $X_nAA'X'_n$  spectrum in which the centre resonance envelope is not resolved, the height of the centre of this envelope relative to the height of the outer resonance lines ( $Y_o$ ) is given by:

$$Y_o = 2^{3-2n} \sum_{x=1}^n (2n-1) C_{(n-x)} \frac{1}{1 + (x - \frac{1}{2})^2 V^2}$$

where  $n$  = number of species of type X

and  $V = \frac{L^2}{|J_{AA'}| \Delta y_{\frac{1}{2}}}$

where  $L = |J_{AX} - J_{AX'}|$

and  $\Delta y_{\frac{1}{2}}$  = width at half height of the outer resonance lines (Hz)

For  $n = 3$

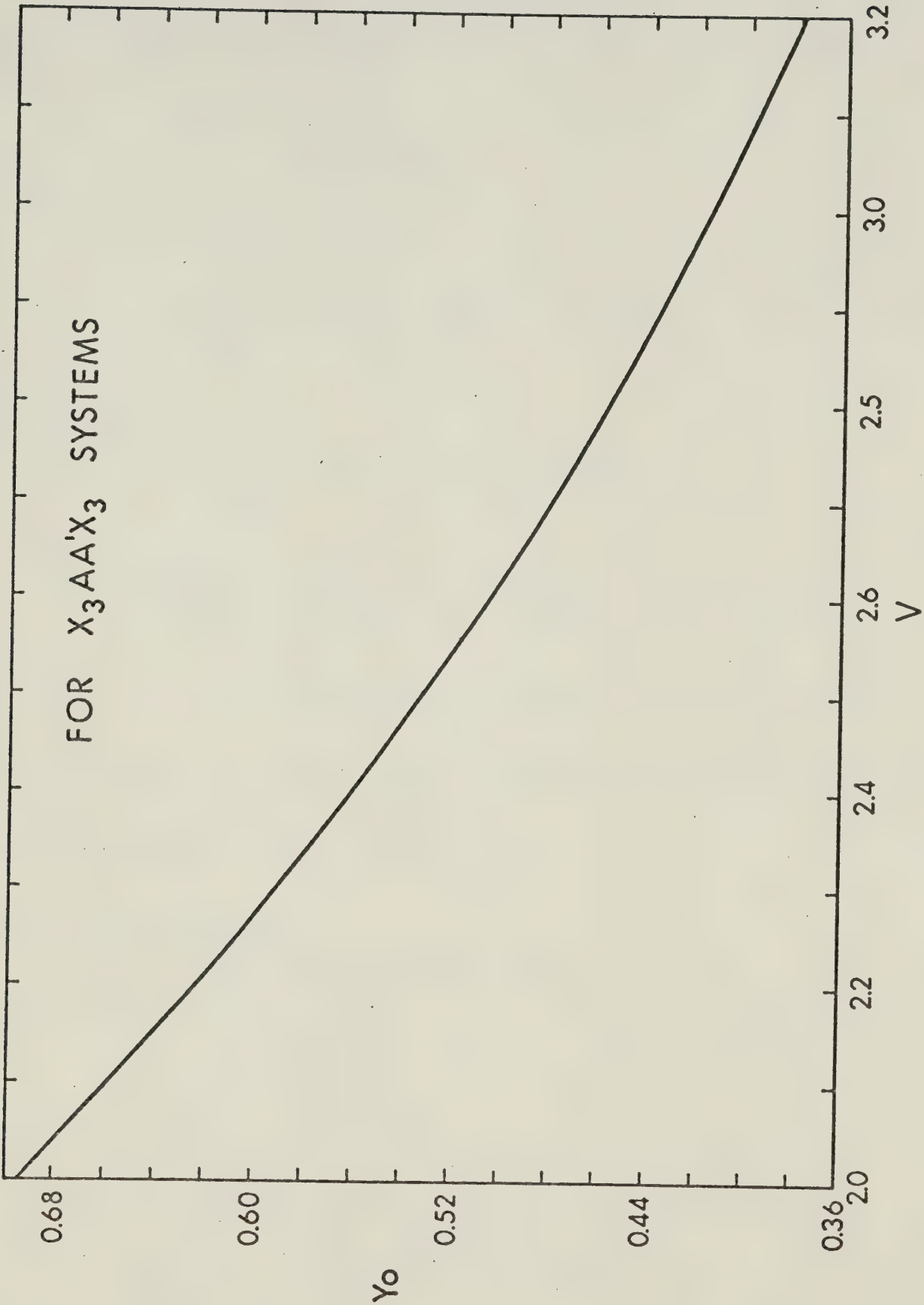
$$Y_o = 2^{-3} \sum_{x=1}^3 {}^5C_{(3-x)} \frac{1}{1 + (x - \frac{1}{2})^2 V^2}$$

$$= \frac{1}{8} \left[ \frac{10}{1 + 0.25V^2} + \frac{5}{1 + 2.25V^2} + \frac{1}{1 + 6.25V^2} \right]$$

This equation has been solved graphically for values of  $V$  in the range 2.0-3.2 (Graph I)



GRAPH I







For  $(\text{Ph}_2\text{MeP})_2\text{Fe}(\text{NO})_2$

$$Y_O = 0.486 \text{ (from nmr spectrum)}$$

and  $V = 2.675$  (from graph)

$$2.675 = \frac{L^2}{|J_{AA'}| \Delta y_{1/2}}$$

$$\Delta y_{1/2} = 1.0 \text{ Hz}$$

$$\frac{L^2}{|J_{AA'}|} = \frac{|J_{AX} - J_{AX'}|^2}{|J_{AA'}|} = 2.68 \text{ Hz}$$

For  $n = 6$

$$Y_O = 2^{-9} \sum_{x=1}^6 {}^{11}C_{(6-x)} \frac{1}{1 + (x - \frac{1}{2})^2 V^2}$$

$$= \frac{1}{512} \left[ \frac{462}{1 + 0.25V^2} + \frac{330}{1 + 2.25V^2} + \frac{165}{1 + 6.25V^2} \right. \\ \left. + \frac{55}{1 + 12.25V^2} + \frac{11}{1 + 20.25V^2} + \frac{1}{1 + 30.25V^2} \right]$$

This equation has been solved graphically for values of  $V$  in the range 2.4-3.4 (Graph II).

For  $(\text{PhMe}_2\text{P})_2\text{Fe}(\text{NO})_2$

$$Y_O = 0.309 \text{ (from nmr spectrum)}$$

and  $V = 3.04$  (from graph)

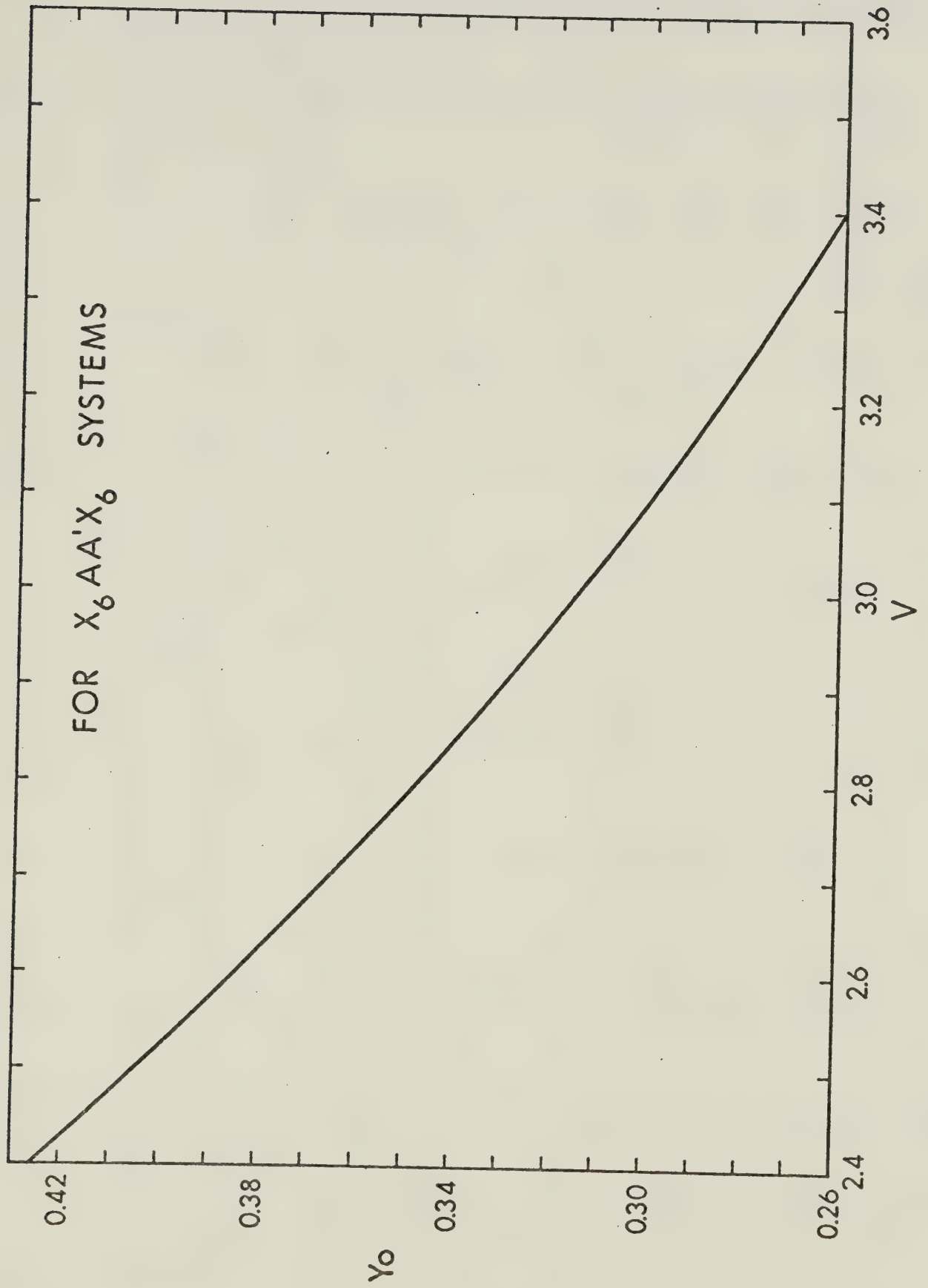
$$3.04 = \frac{L^2}{|J_{AA'}| \Delta y_{1/2}}$$

$$\Delta y_{1/2} = 1.1 \text{ Hz}$$

$$\frac{L^2}{|J_{AA'}|} = \frac{|J_{AX} - J_{AX'}|^2}{|J_{AA'}|} = 3.34 \text{ Hz}$$



GRAPH II





## REFERENCES

1. R.B.King in Adv. Organometal. Chem., 2, 157 (1964)  
F.G.A. Stone and R. West, Eds.
2. T.S. Piper and G. Wilkinson, J.Inorg. Nucl. Chem.,  
3, 104 (1956).
3. R.D. Gorsich, J. Amer. Chem. Soc., 84, 2486 (1962).
4. R.B. King, P.M. Triechel and F.G.A. Stone, Chem. Ind.  
(London), 747 (1961).
5. A. Davison, W. McFarlane, L. Pratt and G. Wilkinson,  
J. Chem. Soc., 3653 (1962).
6. J. P. Collman and W.R. Roper, J. Amer. Chem. Soc.,  
88, 3504 (1966).
- 7 D.M. Adams, D.J. Cook and R.D.W. Kemmitt, Chem.  
Commun., 103 (1966).
8. J.P. Collman and W.R. Roper, Chem. Commun., 244 (1966).
9. E.W. Abel, A. Singh and G.D. Wilkinson, Chem. & Ind.,  
1067 (1959).
10. J.C. Kotz and Pedrotty, J. Organometal. Chem., 22,  
425 (1970).
11. J.C. Kotz and C.D. Turnipseed, Chem. Commun., 41 (1970).
12. J.M. Burlitch and R.B. Petersen, J. Organometal. Chem.,  
24, C65 (1970).
13. D. Cashman and F.J. Lalor, J. Organometal. Chem., 24,  
C29 (1970).
14. F. Ramirez and S. Levy, J. Amer. Chem. Soc., 79, 67  
(1957).



15. R.D. Fischer, Ber., 93, 165 (1960).
16. E.L. Muetterties and C.M. Wright, Quart. Rev., 21, 109 (1967).
17. M.J. Bennett and R. Mason, Proc. Chem. Soc., 273 (1963).
18. D.M. Adams, D.J. Cook and R.D.W. Kemmitt, J. Chem. Soc. (A), 1067 (1968).
19. G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry", Vol. I, 2nd Edition, Academic Press Inc., New York, N.Y., 1963.
20. G.R. Crooks and B.F.G. Johnson, J. Chem. Soc. (A), 1238 (1968).
21. J.M. Enemark and J.A. Ibers, Inorg. Chem., 6, 1575 (1967).
22. N.G. Connelly and L.F. Dahl., Chem. Commun., 880 (1970).
23. N. Okamoto, Ph.D. Thesis, University of Alberta, (1970).
24. R.J. Mawby and G. Wright, J. Organometal. Chem., 21, 169 (1970).
25. W.D. Horrocks, Jr., and R.C. Taylor, Inorg. Chem., 2, 723 (1963).
26. L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand Field Theory", London, Methun & Co. Ltd., (1967) p138.
27. L. Malatesta and A. Araned, J. Chem. Soc., 3803 (1957).
28. W.A. Henderson and C.A. Streuli, J. Amer. Chem. Soc., 82, 5791 (1960).





29. D.W. McBride, S.L. Stafford and F.G.A. Stone, Inorg. Chem., 1, 386 (1962).
30. L.O. Brockway and J.S. Anderson, Trans. Faraday. Soc., 33, 1233 (1937).
31. C.G. Barraclough and J. Lewis, J. Chem. Soc., 4842 (1960)
32. M.A. El-Sayed and H.D. Kaesz, J. Mol. Spectry., 9, 310 (1962).
33. a) E.W. Garbish, Jr., J. Chem. Education, 45, 480 (1968)  
b) F.A.L. Anet, J. Amer. Chem. Soc., 84, 747 (1962).  
c) J.I. Musher and E.J. Corey, Tetrahedron, 18, 791 (1962).
34. R.K. Harris, Can. J. Chem., 42, 2275 (1964).
35. R.J. Abraham and H.J. Bernstein, Can. J. Chem., 39, 216 (1961).
36. J. M. Jenkins and B.L. Shaw, Proc. Chem. Soc., 279 (1963).
37. J.M. Jenkins and B.L. Shaw, J. Chem. Soc., 770 (1966).
38. P.R. Brookes and B.L. Shaw, J. Chem. Soc. (A), 1079 (1967).
39. F.B. Ogilvie, J.M. Jenkins and J.G. Verkade, J. Amer. Chem. Soc., 92, 1916 (1970).
40. J.B. Hendrickson, M.L. Maddox, J.J. Sims and H.D. Kaesz, Tetrahedron, 20, 449 (1964).
41. E.G. Finer and R.K. Harris, Mol. Phys., 12, 457 (1967).
42. J. Lewis, R.S. Nyholm, S.S. Sandu and M.H.B. Stiddard, J. Chem. Soc., 2825 (1964).



43. A.D. Allen and C.V. Senoff, Chem. Commun., 621 (1965)
44. J. Chatt, A.B. Nikolsky, R.L. Richards, J.R. Sanders J.E. Fergusson and J.L. Love, J. Chem. Soc. (A), 1479 (1970).
45. G.W. Parshall, J. Amer. Chem. Soc., 89, 1822 (1967).
46. R.B. King and M.B. Bisnette, J. Amer. Chem. Soc., 86, 5694 (1964).
47. R.B. King and M.B. Bisnette, Inorg. Chem., 5, 300 (1966).
48. A.N. Nesmeyanov, Yu. A. Chapovskii, N.A. Ustynyuk and L.G. Makarova, Acad. Nauk. SSSR Bull., 449 (1968).
49. S. Trofimenko, Inorg. Chem., 8, 2675 (1969).
50. F.J. Lalor and P.L. Pauson, J. Organometal. Chem., 25, C51 (1970).
51. S. Trofimenko, Inorg. Chem., 10, 504 (1971).
52. D.F. Shriver, Accounts of Chem. Res., 3, 231 (1970).
53. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers, 2nd Ed., (1966) ch. 27.
54. K.G. Caulton, R.L. DeKock and R.F. Fenske, J. Amer. Chem. Soc., 92, 515 (1970).
55. J.P. Collman, M. Kubota, F.D. Vastine, J.Y. Sun and J.W. Kang, J. Amer. Chem. Soc., 90, 5430 (1968).
56. A. Roe in "Organic Reactions", John Wiley & Sons, Inc., New York, N.Y., 1967, ch. 4, Vol. 5.



57. R.E. Dessey, R.L. Pohl and R.B. King, J. Amer. Chem. Soc., 88, 5121 (1966).
58. R.B. King, Accounts of Chem. Res., 3, 417 (1970).
59. W. Heiber, J. Sedlemeier and A. Abeck, Ber., 86, 700 (1953).
60. R.B. King, Advan. Chem. Ser. No. 62, 203 (1967).
61. R.B. King, Inorg. Chem., 5, 2227 (1966).
62. R.W. Taft in "Steric Effects in Organic Chemistry", M.S. Newman, Ed., John Wiley & Sons, Inc., New York, N.Y., 1956, ch. 13.
63. F.A. Cotton, T.G. Dunne and J.S. Wood, Inorg. Chem., 4, 318 (1965).
64. G. Balz and G. Schiemann, Ber., 60, 1186 (1927).
65. M.F.W. Dunker, E.B. Starkey and G.L. Jenkins, J. Amer. Chem. Soc., 58, 2308 (1936).
66. E. Bergmann and A. Bondi, Ber., 64, 1455 (1931).
67. G. Schiemann and E. Bolstad, Ber., 61, 1403 (1928).

















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